

Chapter 4

Biorenewable Liquid Fuels

4.1 Introduction to Biorenewable Liquid Fuels

The aim of this chapter is to provide a global approach on liquid biofuels such as bioethanol, biodiesel, vegetable oils, bio-oils, and other biorenewable liquid fuels for the future of energy for transportation. It is possible that sugar cane, corn, wood, straw, and even household wastes may be economically converted to bioethanol. Bioethanol is derived from alcoholic fermentation of sucrose or simple sugars, which are produced from biomass by a hydrolysis process. Biodiesel is an environmentally friendly alternative liquid fuel that can be used in any diesel engine without modification. There has been renewed interest in the use of vegetable oils for making biodiesel due to its less polluting and renewable nature as against conventional petroleum diesel fuel (Demirbas, 2008).

Due to its environmental merits, the share of biofuel such as bioethanol and biodiesel in the automotive fuel market will grow fast in the next decade. An important reason for interest in renewable energy sources is the concern for the greenhouse effect. Biorenewable liquid fuels have gained a lot of attention due to their environmental and technological advantages. Development of ethanol as a motor fuel can work to fulfill this commitment. Greenhouse gas emission reductions should be estimated on an annual basis. Where the levels from year to year vary significantly these should be specified on an annual basis. If ethanol from biomass is used to drive a light-duty vehicle, the net CO₂ emission is less than 7% of that from the same car using reformulated gasoline (Bergeron, 1996).

The most important biorenewable liquid fuels are bioethanol and biodiesel made from plant material and recycled elements of the food chain. Biodiesel is a diesel alternative. Bioethanol is a petrol additive/substitute. Biorenewable fuels are safely and easily biodegradable and so are particularly well suited to the environment. Biodiesel, a biofuel that can replace directly petroleum-derived diesel without engine modifications, has gained a lot of attention due to its environmental and technological advantages. These advantages include its being from

a renewable source, completely biodegradable, cleaner burning than petroleum-based diesel, low in sulfur, and resulting in CO₂ recycling.

4.1.1 Evaluation of Gasoline-Alcohol Mixtures as Motor Fuel Alternatives

Production of motor fuel alternatives from biomass materials is an important application area of biotechnological methods. Table 4.1 shows potential and available motor fuels. Biorenewable sourced motor fuel alternatives are:

1. Gasoline-alcohol mixtures
2. Alcohol substituting gasoline
3. Gasoline-vegetable oil mixtures
4. Diesel fuel-vegetable oil mixtures
5. Vegetable oil substituting diesel fuel.

The application of alcohol and gasoline-alcohol mixtures in gasoline (Otto) engines began in the first half of the 20th century. It is possible to find information about various studies on the change in octane numbers of gasoline-alcohol mixtures, composition of the exhaust gases, motor tests, and about the materials used in constructing the engines. Between 1980 and 1985 studies intensified on solving the phase separation problem of gasoline-alcohol mixtures.

In gasoline-alcohol mixtures ethanol and methanol are generally used, and in gasoline engine mixtures containing 20% or less alcohol by volume can be used without altering the construction of the engine. Because of the hygroscopic properties of ethanol and methanol the gasoline-alcohol mixtures are in fact ternary mixtures composed of gasoline-alcohol and water. In the evaluation of such mixtures as motor fuel there is the phase separation problem, which depends on several factors. It can be seen in the literature that there have been numerous attempts to overcome this problem (Mislavskaya *et al.*, 1982; Osten and Sell, 1983).

In gasoline-methanol mixtures containing 0.1% water i-propanol is added to the environment (medium) in order to decrease the phase separation temperature, and

Table 4.1 Potential and available motor fuels

Fuel type	Available motor fuel
Traditional fuels	Diesel and gasoline
Oxygenated fuels	Ethanol 10% (E10), methanol, methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), tertiary butyl alcohol (TBA), and tertiary amyl methyl ether (TAME)
Alternative fuels	Liquefied petroleum gases (LPG), ethanol, 85% (E85), ethanol, 95% (E95), methanol, 85% (M85), methanol, neat (M100), compressed natural gas (CNG), liquefied natural gas (LNG), biodiesel (BD), hydrogen, electricity

fuels containing different ratios of gasoline-methanol-i-propanol and water are composed, which are proved to be stable in the climatic conditions. An increase in the aromatic character of the gasoline, a decrease in the water content of the mixture, an increase in the amount of the additive used results in a decrease in the phase separation temperature of the mixture. In gasoline-ethanol mixtures the additive used is also i-propanol. In gasoline-alcohol mixtures various additives like i-propanol, n-butanol, i-butanol, and i-amylalcohol are used.

4.1.2 Evaluation of Vegetable Oils and Diesel Fuel Mixtures as Motor Fuel Alternatives

Since the 1980s important progress has been made on evaluating some low grade oils, oil production wastes, and residues as motor fuel (Pryor *et al.*, 1983). However, direct usage of vegetable oils causes a number of problems concerning the engine because of their high viscosity and the excessive carbonaceous deposits left in the cylinders and on the injector nozzles. Therefore, chemical conversion of vegetable oils was suggested. In order to lower the viscosities and flash points of vegetable oils the transesterification method has been applied and it is reported that the alcoholysis products of soybean, sunflower, rapeseed, and used frying oils were proposed as diesel fuel alternatives.

The deregulation of domestic crude oil prices and the formation of OEC have been largely responsible for high fuel prices. The farmer is highly dependent on diesel fuel for crop production. Alternative fuels such as vegetable oils may help ease the petroleum dependence of farmers. Recently, the demand for crude oil has decreased because of conservation practices, but ultimately a liquid fuel resource problem exists (Pryor *et al.*, 1983).

4.2 Bioalcohols

The alcohols that can be used for motor fuels are methanol (CH_3OH), ethanol ($\text{C}_2\text{H}_5\text{OH}$), propanol ($\text{C}_3\text{H}_7\text{OH}$), and butanol ($\text{C}_4\text{H}_9\text{OH}$). However, only first two are technically and economically suitable as fuels for internal combustion engines (ICEs). Main commercial bioalcohols from renewable feedstocks are bioethanol and biomethanol in the world's energy marketing. Bioethanol currently accounts for more than 94% of global biofuel production, with the majority coming from sugarcane. About 60% of global bioethanol production comes from sugarcane and 40% from other crops. Brazil and the United States are the world leaders, which together accounted for about 70% of the world bioethanol production exploiting sugarcane and corn respectively. Ethanol was used in Germany and France as early as 1894 by the then incipient industry of internal combustion engines. Brazil

has utilized ethanol as a fuel since 1925. Currently, ethanol is produced from sugar beets and from molasses. A typical yield is 72.5 liters of ethanol *per* ton of sugar cane. Modern crops yield 60 tons of sugar cane *per* hectare of land. Production of ethanol from biomass is one way to reduce both the consumption of crude oil and environmental pollution. The use of gasohol (an ethanol and gasoline mixture) as an alternative motor fuel has been steadily increasing in the world for a number of reasons. Domestic production and use of ethanol for fuel can decrease dependence on foreign oil, reduce trade deficits, create jobs in rural areas, reduce air pollution, and reduce global climate change carbon dioxide build-up (Bala, 2005).

4.2.1 *Alternate Fuels to Gasoline*

Gasoline is a blend of hydrocarbons with some contaminants, including sulfur, nitrogen, oxygen, and certain metals. The four major constituent groups of gasoline are olefins, aromatics, paraffins, and naphthenes. The important characteristics of gasoline are density, vapor pressure, distillation range, octane, and chemical composition. To be attractive, a motor gasoline must have (a) desirable volatility, (b) antiknock resistance (related to octane rating), (c) good fuel economy, (d) minimal deposition on engine component surfaces, and (e) complete combustion and low pollutant emissions (Chigier, 1981).

Alternative fuels for Otto engines or light-duty vehicles (LDVs; cars and light trucks) contain (1) reformulated gasoline, (2) compressed natural gas, (3) methanol and ethanol, (4) liquid petroleum gas, (5) liquefied natural gas, (6) Fischer–Tropsch liquids from natural gas, (7) hydrogen, and (8) electricity. The electricity can be obtained from (a) spark ignition port injection engines, (b) spark ignition direct injection engines, (c) compression ignition engines, (d) electric motors with battery power, (e) hybrid electric propulsion options, and (f) fuel cells (Demirbas, 2005a).

Figure 4.1 shows the whole sale prices of a number of possible alternative fuels on an energy equivalent basis compared to conventional gasoline (AIChE, 1997). Only compressed natural gas (CNG) and liquid petroleum gas (LPG) appear to have some economic advantage relative to gasoline while ethanol, methanol, and electricity are at a severe economic disadvantage (Piel, 2001).

The most commonly used measure of a gasoline's ability to burn without knocking is its octane number. Table 4.2 shows hydrocarbon octane numbers. By 1922 a number of compounds had been discovered that were able to increase the octane number of gasoline. Adding as little as 6 mL of tetraethyl lead (Fig. 4.2) to a gallon of gasoline, for example, can increase the octane number by 15 to 20 units. This discovery gave rise to the first "ethyl" gasoline, and enabled the petroleum industry to produce aviation gasolines with octane numbers greater than 100. The octane numbers and some properties of common fuels are given in Table 4.3. As seen in Table 4.3, the octane numbers of ethanol and methanol are 107 and 112, respectively.

About 10% of the product of the distillation of crude oil is a fraction known as straight-run gasoline. Straight-run gasoline burns unevenly in high-compression

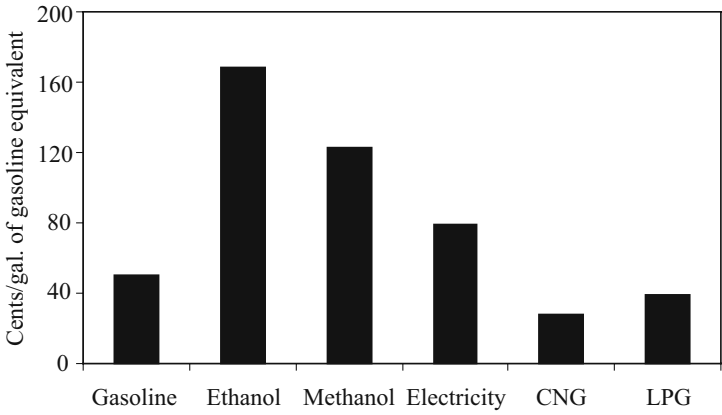


Fig. 4.1 Economics of gasoline alternative fuels

Table 4.2 Hydrocarbon octane numbers

Hydrocarbon	Octane Number (ON)
Heptane	0
2-Methylheptane	23
Hexane	25
2-Methylhexane	44
1-Heptene	60
Pentane	62
1-Pentene	84
Butane	91
Cyclohexane	97
2,2,4-Trimethylpentane (isooctane)	100
Benzene	101
Toluene	112

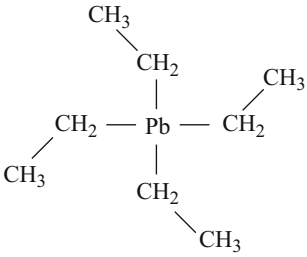


Fig. 4.2 Chemical structure of tetraethyl lead

Table 4.3 Octane number and some properties of common fuels

Fuel property	Ethanol	Gasoline	Diesel No. 2	Isooctane	Methanol
Cetane number	—	—	50	—	5
Octane number	96	—	—	100	112
Auto-ignition temperature (K)	644	588	—	530	737
Latent heat of vaporization (MJ/Kg)	0.35	0.22	—	0.26	1.18
Lower heating value (MJ/Kg)	44.0	42.6	—	45.0	19.9
					26.7

engines, producing a shock wave that causes the engine to “knock” or “ping”. The relationship between knocking and the structure of the hydrocarbons in gasoline is summarized in the following general rules.

- Branched alkanes and cycloalkanes burn more evenly than straight-chain alkanes.
- Short alkanes (C_4H_{10}) burn more evenly than long alkanes (C_7H_{16}).
- Alkenes burn more evenly than alkanes.
- Aromatic hydrocarbons burn more evenly than cycloalkanes.

4.3 Bioethanol

Nowadays ethanol is the most popular fuel. Bioethanol is ethyl alcohol, grain alcohol, or chemically C_2H_5OH or $EtOH$. The use of ethanol as a motor fuel has as long a history as the car itself. Ethanol can be produced from cellulose feedstocks such as corn stalks, rice straw, sugar cane, bagasse, pulpwood, switchgrass, and municipal solid waste is called bioethanol. Bioethanol is a renewable green fuel. Utilization of ethyl alcohol as engine fuel is one way to reduce both the consumption of crude oil and environmental pollution. Primary consideration involves the production of ethyl alcohol from renewable resources and determination of the economic and technical feasibility of using alcohol as an automotive fuel blended with gasoline. An important reason for interest in renewable energy sources is the concern for the greenhouse effect. Development of ethanol as a motor fuel can work to fulfill this commitment. Greenhouse gas emission reductions should be estimated on an annual basis. Where the levels from year to year vary significantly these should be specified on an annual basis. If ethanol from biomass is used to drive a light-duty vehicle, the net CO_2 emission is less than 7% of that from the same car using reformulated gasoline (Bergeron, 1996).

4.3.1 Synthetic Ethanol Production Processes

The hydration of ethylene is the oldest process among the two major ethanol production methods from ethylene ($CH_2 = CH_2$), and started more than 100 years ago.

The ethanol is prepared from ethylene in a three-step process using sulfuric acid (H_2SO_4). In the first step, the hydrocarbon feedstock containing 35–95% ethylene is exposed to 95–98% sulfuric acid in a column reactor to form monosulfate:

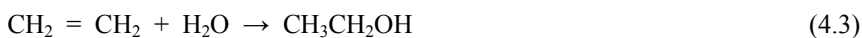


It is subsequently hydrolyzed with enough water to give 50–60% aqueous sulfuric acid solution:



The ethanol is then separated from the dilute sulfuric acid in a stripper column. The last step of this process is to concentrate the sulfuric acid and recycle to the process.

In the direct hydration process, an ethylene-rich gas is combined with water and passes through a fixed-bed catalyst reactor, in which ethanol is formed according to the following reaction (Nelson and Courter, 1954):



The ethanol is then recovered in a distillation system.

Ethanol can be obtained from acetylene process in the presence of a proper catalyst such as H_2SO_4 and HgSO_4 ; acetylene/ethyne reacts with water to yield acetaldehyde:



Acetaldehyde can be readily reduced by catalytic hydrogenation to ethyl alcohol:



The classical catalyst is octacarbonyldicobalt, $\text{Co}_2(\text{CO})_8$, formed by reaction of metallic cobalt with carbon monoxide.

4.3.2 *Production of Ethanol from Biomass*

Ethanol from biorenewable feedstocks has the potential to contribute substantially to bioethanol for transportation. In the process evaluated, prehydrolysis with dilute sulfuric acid is employed to hydrolyze hemicellulose and make the cellulose more accessible to hydrolysis by enzymes. Residual biomass from hydrolysis and extraction of carbohydrates can be burned in a power plant to generate electricity and process steam.

Carbohydrates in plant materials can be converted to sugars by a hydrolysis process. Fermentation is an anaerobic biological process in which sugars are converted to alcohol by the action of microorganisms, usually yeast. The resulting alcohol is bioethanol. The value of any particular type of biomass as feedstock for fermentation depends on the ease with which it can be converted to sugars. Bio-

ethanol and the biorefinery concept are closely linked. It is possible that wood, straw, and even household wastes may be economically converted to bioethanol.

The corn-starch-to-fuel ethanol industry has matured during the past 30 years by bioethanol research. Most bioethanol researchers are focusing on the challenge of producing bioethanol from lignocellulosic biomass instead of corn starch. Toward this end, researchers have already developed an effective technology to thermochemically pretreat biomass; to hydrolyze hemicellulose to break it down into its component sugars and open up the cellulose to treatment; to enzymatically hydrolyze cellulose to break it down to sugars; and to ferment both five-carbon sugars from hemicellulose and six-carbon sugars from cellulose. Figure 4.3 shows the flow chart for the production of bioethanol from cereal grain or straw.

Bioethanol can be produced from a large variety of carbohydrates with a general formula of $(\text{CH}_2\text{O})_n$. The chemical reaction is composed of enzymatic hydrolysis of sucrose followed by fermentation of simple sugars. Fermentation of sucrose is performed using commercial yeast such as *Saccharomyces cerevisiae*. First, the invertase enzyme in the yeast catalyzes the hydrolysis of sucrose to convert it into glucose and fructose.



Second, zymase, another enzyme also present in the yeast, converts the glucose and the fructose into ethanol.



The gluco-amylase enzyme converts the starch into D-glucose. The enzymatic hydrolysis is then followed by fermentation, distillation, and dehydration to yield

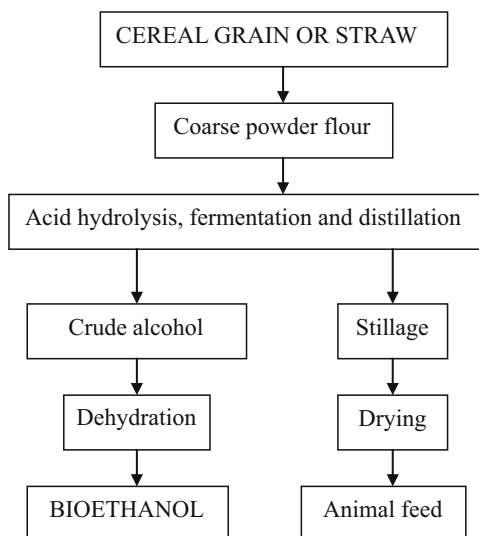


Fig. 4.3 Flow chart for the production bioethanol from cereal grain or straw

anhydrous bioethanol. Corn (60–70% starch) is the dominant feedstock in the starch-to-bioethanol industry worldwide.

Cellulose hydrolysis produces glucose, which is readily fermented with existing organisms in much the same way as has been done for centuries. Hemicelluloses hydrolysis produces both hexose and pentose sugars: mannose, galactose, xylose, and arabinose that are not all fermented with existing strains.

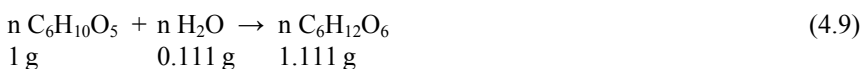
The hemicelluloses fraction typically produces a mixture of sugars including xylose, arabinose, galactose, and mannose. These are both pentosans: xylose and arabinose, and hexosans: galactose and mannose. The quantities are dependent on the material and also the growing environment and storage history of the material.

The amount of product formed *per* unit of substrate consumed by the organism is a useful way to refer to yields. The yields of fermentation are expressed on either molar or weight basis. In this case the primary stoichiometric equations for the bioethanol production are as follows.

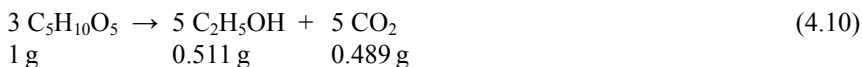
Pentosan to pentose:



Hexosan to hexose:



Pentose and hexose to bioethanol, 0.511 grams *per* gram hexose or pentose:



A reduction in yield below the theoretical value always occurs since the microorganism requires a portion of the substrate for cell growth and maintenance. For *E. coli* and *S. cerevisiae* these values are approximately 0.054 and 0.018 grams of glucose/g dry cell weight-hour, respectively (Roels and Kossen, 1978).

Microorganisms for ethanol fermentation can best be described in terms of their performance parameters and other requirements such as compatibility with existing products, processes, and equipment. The performance parameters of fermentation are: temperature range, pH range, alcohol tolerance, growth rate, productivity, osmotic tolerance, specificity, yield, genetic stability, and inhibitor tolerance.

4.3.3 Sugars from Biomass by Hydrolysis

Hydrolysis breaks down the hydrogen bonds in the hemicelluloses and cellulose fractions into their sugar components: pentoses and hexoses. These sugars can

then be fermented into ethanol. Pretreatment methods refer to the solubilization and separation of one or more of the four major components of biomass to make the remaining solid biomass more accessible to further chemical or biological treatment.

After the pretreatment process, there are two types of processes to hydrolyze the cellulosic biomass for fermentation into ethanol. The most commonly applied methods can be classified in two groups: chemical hydrolysis and enzymatic hydrolysis.

Both enzymatic and chemical hydrolyses require a pretreatment to increase the susceptibility of cellulosic materials. In the chemical hydrolysis, the pretreatment and the hydrolysis may be carried out in a single step. There are two basic types of acid hydrolysis processes commonly used: dilute acid and concentrated acid, each with variations.

Dilute acid processes are conducted under high temperature and pressure, and have reaction times in the range of seconds or minutes, which facilitates continuous processing. Most dilute acid processes are limited to a sugar recovery efficiency of around 50%. The reason for this is that at least two reactions are part of this process. Not only does sugar degradation reduce sugar yield, but the furfural and other degradation products can be poisonous to the fermentation microorganisms. The biggest advantage of dilute acid processes is their fast rate of reaction, which facilitates continuous processing.

Since 5-carbon sugars degrade more rapidly than 6-carbon sugars, one way to decrease sugar degradation is to have a two-stage process. The first stage is conducted under mild process conditions to recover the 5-carbon sugars while the second stage is conducted under harsher conditions to recover the 6-carbon sugars. The primary advantage of the concentrated process is the high sugar recovery efficiency (Demirbas, 2004a).

4.3.3.1 Dilute Acid Hydrolysis

The dilute acid process is conducted under high temperature and pressure, and has a reaction time in the range of seconds or minutes, which facilitates continuous processing. As an example, using a dilute acid process with 1% sulfuric acid in a continuous flow reactor at a residence time of 0.22 minutes and a temperature of 510 K with pure cellulose provided a yield over 50% sugars. The combination of acid and high temperature and pressure dictate special reactor materials, which can make the reactor expensive. The first reaction converts the cellulosic materials to sugar and the second reaction converts the sugars to other chemicals.

The biggest advantage of dilute acid processes is their fast rate of reaction, which facilitates continuous processing. Since 5-carbon sugars degrade more rapidly than 6-carbon sugars, one way to decrease sugar degradation is to have a two-stage process. The first stage is conducted under mild process conditions to recover the 5-carbon sugars while the second stage is conducted under harsher conditions to recover the 6-carbon sugars.

4.3.3.2 Concentrated Acid Hydrolysis

Concentrated acid hydrolysis uses relatively mild temperatures, and the only pressures involved are those created by pumping materials from vessel to vessel. Reaction times are typically much longer than for dilute acid. This method generally uses concentrated sulfuric acid followed by a dilution with water to dissolve and hydrolyze or convert the substrate into sugar. This process provides a complete and rapid conversion of cellulose to glucose and hemicelluloses to 5-carbon sugars with little degradation. The critical factors needed to make this process economically viable are to optimize sugar recovery and cost effectively recovers the acid for recycling.

The primary advantage of the concentrated acid process is the potential for high sugar recovery efficiency. Table 4.4 shows the yields of bioethanol by concentrated sulfuric acid hydrolysis from cornstalks. The acid and sugar are separated *via* ion exchange and then acid is re-concentrated *via* multiple effect evaporators. The low temperatures and pressures employed allow the use of relatively low cost materials such as fiberglass tanks and piping. The low temperatures and pressures also minimize the degradation of sugars. Unfortunately, it is a relatively slow process and cost effective acid recovery systems have been difficult to develop. Without acid recovery, large quantities of lime must be used to neutralize the acid in the sugar solution. This neutralization forms large quantities of calcium sulfate, which requires disposal and creates additional expense.

Table 4.4 Yields of bioethanol by concentrated sulfuric acid hydrolysis from cornstalks (% dry weight)

<i>Amount of cornstalk (kg)</i>	1000
Cellulose content (kg)	430
Cellulose conversion and recovery efficiency	0.76
Ethanol stoichiometric yield	0.51
Glucose fermentation efficiency	0.75
Ethanol yield from glucose (kg)	130
<i>Amount of cornstalk (kg)</i>	1000
Hemicelluloses content (kg)	290
Hemicelluloses conversion and recovery efficiency	0.90
Ethanol stoichiometric yield	0.51
Xylose fermentation efficiency	0.50
Ethanol yield from xylose (kg)	66
<i>Total ethanol yield from 1000 kg of cornstalk</i>	196 kg (225.7 L = 59 gal)

Source: Demirbas, 2005b

4.3.3.3 Enzymatic Hydrolysis

Another basic method of hydrolysis is enzymatic hydrolysis. Enzymes are naturally occurring plant proteins that cause certain chemical reactions to occur. However, for enzymes to work, they must obtain access to the molecules to be hydro-

lyzed. There are two technological developments: enzymatic and direct microbial conversion methods. Another basic method of hydrolysis is enzymatic hydrolysis.

The chemical pretreatment of the cellulosic biomass is necessary before enzymatic hydrolysis. The first application of enzymatic hydrolysis was used in separate hydrolysis and fermentation steps. Enzymatic hydrolysis is accomplished by cellulolytic enzymes. Different kinds of “cellulases” may be used to cleave the cellulose and hemicelluloses. A mixture of endoglucanases, exoglucanases, β -glucosidases, and cellobiohydrolases is commonly used (Ingram and Doran, 1995; Laymon *et al.*, 1996). The endoglucanases randomly attack cellulose chains to produce polysaccharides of shorter length, whereas exoglucanases attach to the non-reducing ends of these shorter chains and remove cellobiose moieties. β -glucosidases hydrolyze cellobiose and other oligosaccharides to glucose (Philippidis and Smith, 1995).

For enzymes to work efficiently, they must obtain access to the molecules to be hydrolyzed. This requires some kind of pretreatment process to remove hemicelluloses and break down the crystalline structure of the cellulose or removal of the lignin to expose hemicelluloses and cellulose molecules.

Hydrolysis is often used to pretreat lignocellulosic feedstocks to break down the cellulose and hemicelluloses from the lignocellulose and break down the compounds into simple sugars. Hydrolysis can be catalyzed by use of acids (either strong or weak), enzymes, and/or hydrothermal means, the latter including hot water and supercritical methods. Figure 4.4 shows a schematic flow diagram of enzymatic hydrolysis process.

Cellulosic materials are comprised of lignin, hemicelluloses, and cellulose and are thus sometimes called lignocellulosic materials. Cellulose molecules consist of long chains of glucose molecules (6-carbon sugars) as do starch molecules, but have a different structural configuration. Since pentose molecules (5-carbon sugars) comprise a high percentage of the available sugars, the ability to recover and ferment them into ethanol is important for the efficiency and economics of the process.

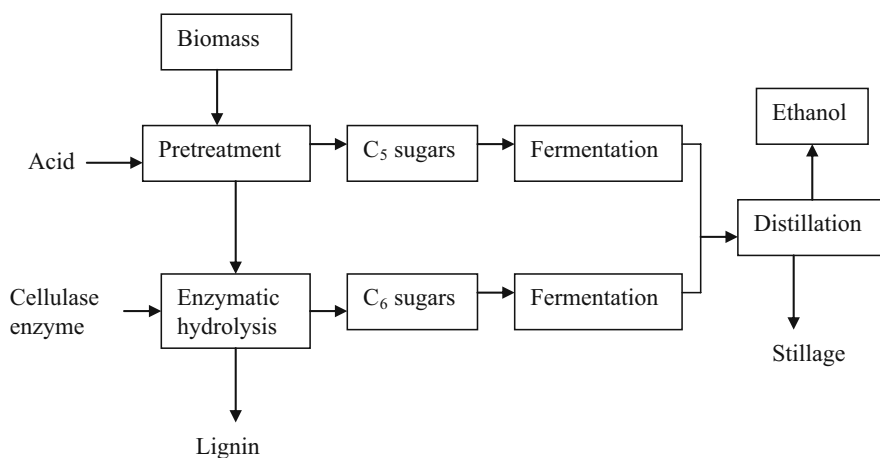


Fig. 4.4 Schematic flow diagram of the enzymatic hydrolysis process

Recently, special microorganisms have been genetically engineered that can ferment 5-carbon sugars into ethanol with relatively high efficiency. Bacteria have drawn special attention from researchers because of their speed of fermentation.

The biggest advantage of dilute acid processes is their fast rate of reaction, which facilitates continuous processing. Since 5-carbon sugars degrade more rapidly than 6-carbon sugars, one way to decrease sugar degradation is to have a two-stage process. The first stage is conducted under mild process conditions to recover the 5-carbon sugars while the second stage is conducted under harsher conditions to recover the 6-carbon sugars.

A new generation of enzymes and enzymes production technology is needed to cost-effectively hydrolyze cellulose to glucose. Technical barriers for enzymatic hydrolysis include: low specific activity of current commercial enzymes, high cost of enzyme production, and lack of understanding of enzyme biochemistry and mechanistic fundamentals.

Biomass can be hydrolyzed to create fermentable sugars for producing ethanol. The lignin component is also unconvertible in a hydrolysis and fermentation system. Sugars can also be converted to levulinic acid and citric acid. Levulinic acid is a versatile chemical that is a precursor to other specialty chemicals, fuels and fuels additives, herbicides, and pesticides. The largest application for citric acid is in the beverage industry, which accounts for about 45% of the market for this product. Citric acid is also used in a wide variety of candies, frozen foods, and processed cheeses, and as a preservative in canned goods, meats, jellies, and preserves. Residual acids in the sugar stream can be neutralized using lime. The use of lime as a neutralizing agent yields gypsum, which can be sold as a soil amendment or to wallboard manufacturers.

The first application of enzymatic hydrolysis was used in separate hydrolysis and fermentation steps. Enzymatic hydrolysis is accomplished by cellulolytic enzymes. Different kinds of cellulases may be used to cleave the cellulose and hemicelluloses. A mixture of endoglucanases, exoglucanases, β -glucosidases, and cellobiohydrolases is commonly used. The endoglucanases randomly attack cellulose chains to produce polysaccharides of shorter length, whereas exoglucanases attach to the non-reducing ends of these shorter chains and remove cellobiose moieties. β -glucosidases hydrolyze cellobiose and other oligosaccharides to glucose.

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4.3.4 Bioethanol Production by Fermentation of Carbohydrates

Fermentation using genetically engineered yeast or bacteria will utilize all five of the major biomass sugars: glucose, xylose, mannose, galactose, and arabinose. Ethanol may be produced by direct fermentation of sugars, or from other carbohy-

drates that can be converted to sugar, such as starch and cellulose. Fermentation of sugars by yeast, the oldest synthetic chemical process used by man, is still of enormous importance for the preparation of ethyl alcohol. Sugars come from a variety of sources, mostly molasses from sugar cane, or starch obtained from various grains; the name "grain alcohols" has been given to ethyl alcohol for this reason. The raw materials are classified into three categories of agricultural raw materials: (1) simple sugars from sugar cane, sugar beet, molasses, and fruit; (2) starch from grains, potatoes, and root crops; and (3) cellulose from wood, agricultural residue, municipal solid wastes, waste papers, and crop residues.

Some sugars can be converted directly to ethanol, whereas starch and cellulose must first be hydrolyzed to sugar before conversion to ethanol. Most of the polymeric raw materials are available at prices lower than refined sugars. However, transportation costs of the raw materials make it necessary to use locally available raw material. Consequently, each country may preferably develop ethanol production based on the available raw material in that country (Taherzadeh, 1999).

The fermentation method generally uses three steps: (a) the formation of a solution of fermentable sugars, (b) the fermentation of these sugars to ethanol, and (c) the separation and purification of the ethanol, usually by distillation.

Fermentation involves microorganisms that use the fermentable sugars for food and in the process produces ethyl alcohol and other byproducts. These microorganisms can typically use the 6-carbon sugars, one of the most common being glucose. Therefore, cellulosic biomass materials containing high levels of glucose or precursors to glucose are the easiest to convert to ethanol. Microorganisms, termed ethanologens, presently convert an inadequate portion of the sugars from biomass to ethanol. Although fungi, bacteria, and yeast microorganisms can be used for fermentation, specific yeast (*Saccharomyces cerevisiae* also known as Bakers' yeast) is frequently used to ferment glucose to ethanol.

Operating temperatures are less than desired and the organism performance can be inhibited by components inherent in the process. Three recombinant fermentation strains were considered to be candidates for short term improvement by the participants: *Saccharomyces*, *E. Coli* and *Zymomonas*. There is a clear preference for yeast by the existing grain ethanol producers, particularly *Saccharomyces*. This yeast is widely used, known and fits existing equipment.

The hemicelluloses fraction typically produces a mixture of sugars including xylose, arabinose, galactose, and mannose. These are both pentosans: xylose and arabinose, and hexosans: galactose, and mannose. The quantities are dependent on the material and also the growing environment and storage history of the material.

A reduction in yield below the theoretical value always occurs since the microorganism requires a portion of the substrate for cell growth and maintenance. For *E. coli* and *S. cerevisiae* these values are approximately 0.054 and 0.018 grams of glucose/g dry cell weight-hour respectively (Demirbas, 2004a).

4.3.4.1 Fungal Enzymes to Convert Biomass to Bioethanol

Bioethanol production from biomass is one such already proven industrial process for renewable energy production. Bioethanol can be directly mixed with petrol and used in today's cars, or converted to electricity. Currently there are two type blends of ethanol/gasoline on the market: blends of 10% ethanol and 90% gasoline (E10) and blends of 85% ethanol and 15% gasoline (E85). In the US, many states currently mandate E10 in gasoline. It is generally accepted that bioethanol gives a 70% carbon dioxide reduction, which means 7% in an E10 blend or 50% in an E85 blend. Increased bioethanol usage may reduce U.S. greenhouse-gas emissions to 1.7 billion tons/year. Recent researches have established that polysaccharides in biomass can be hydrolyzed enzymatically into glucose sugar that is fermented to bioethanol.

When manufactured from agricultural sources, like corn or wood, ethanol is commonly referred to as bioethanol. Theoretically, bioethanol production should be able to yield 0.5 g of ethanol *per* gram of raw biomass, which translates into an energy recovery of approximately 90%. Corn is a common substrate for bioethanol manufacture because the process is relatively free of technical obstacles. Microorganisms are involved in the transformation of corn to bioethanol in two ways: they catalyze the hydrolysis of starches using amylases and amyloglucosidases and they ferment the resulting sugars to bioethanol. The fermentation step is generally carried out by yeast, but certain strains of bacteria, including *Zymomonas mobilis* and recombinant strains of *Escherichia coli* and *Klebsiella oxytoca*, are also capable of producing high yields of bioethanol.

Because bioethanol is a liquid, bioethanol fits into the current fuel infrastructure, although transport requires special handling to prevent water accumulation. Bioethanol can be cost-competitive with petroleum. However, using solid substrates in converting lignocellulose to sugars poses a dilemma in bioethanol production. Cellulose and lignocellulose are in much greater supply than starch and sugars and are, therefore, preferred substrates for ethanol production. However, producing ethanol from cellulose and lignocellulose is comparatively difficult and expensive.

Lignocellulose includes such diverse sources as switchgrass, cornstalks, and wood chips. Fungal enzymes and fermentative yeasts are then used to transform lignocellulose first to sugars and then to bioethanol. The low lignocellulose reactivity limits the production of bioethanol. The expense of enzyme production is the biggest economic barrier to lignocellulose conversion to bioethanol.

Biological pretreatments use fungi to solubilize the lignin. Biodelignification is the biological degradation of lignin by microorganisms. Biodelignification will be a useful delignification method in the future, although at that time it was inadequate and expensive, required a long process time and the microorganisms were poisoned by lignin derivatives. These technologies could greatly simplify pretreatment, but the rates are slow, yields are low, and there is little experience with such approaches.

Recent research has focused on enzyme catalysts called *cellulases* that can attack these chains more efficiently, leading to very high yields of fermentable sugars. Fungal *cellulases* and *beta-glucosidases* produced in separate aerobic reactors can be extracted in very high yields, but because these enzymes have low specific activities, they must be used in large quantities to achieve lignocellulose conversion.

Fungi produce a plethora of enzymes that are used to degrade complex polysaccharides and proteins into simpler sugars and amino acids, and are long established as a key source of a wide variety of industrially important enzymes. Some of these enzymes have already been harnessed in releasing fermentable sugars from a variety of biomass feedstocks, including waste paper, food stuffs, cereals, sugar crops, grains, and woods.

Both bacteria and fungi can produce cellulases for the hydrolysis of lignocellulosic materials. These microorganisms can be aerobic or anaerobic, mesophilic or thermophilic. Bacteria belonging to *Clostridium*, *Cellulomonas*, *Bacillus*, *Thermomonospora*, *Ruminococcus*, *Bacteriodes*, *Erwinia*, *Acetovibrio*, *Microbispora*, and *Streptomyces* can produce cellulases (Sun, 2002).

The widely accepted mechanism for enzymatic cellulose hydrolysis involves synergistic actions by endoglucanases or endo-1,4- β -glucanases (EG), exoglucanases or cellobiohydrolases (CBH), and β -glucosidases (BGL). EG play an important role in cellulose hydrolysis by cleaving cellulose chains randomly and thus encouraging strong degradation. EG hydrolyze accessible intramolecular β -1,4-glucosidic bonds of cellulose chains randomly to produce new chain ends; exoglucanases processively cleave cellulose chains at the ends to release soluble cellobiose or glucose; and BGL hydrolyze cellobiose to glucose in order to eliminate cellobiose inhibition (Zhang *et al.*, 2006). BGL complete the hydrolysis process by catalyzing the hydrolysis of cellobiose to glucose.

Filamentous fungi are the major source of *cellulases* and *hemicellulases*. Mutant strains of *Trichoderma sp.* (*T. viride*, *T. reesei*, *T. longibrachiatum*) have long been considered to be the most productive and powerful destroyers of crystalline cellulose (Gusakov *et al.*, 2005). CBH I and CBH II are the major *T. reesei* enzymes; the content of CBH I comprises up to 60% of the total cellulolytic protein; whereas, the content of CBH II is about 20% (Gusakov *et al.*, 2005). Similarly, EG I and EG II are the dominant endoglucanases in *T. reesei*, and presumably acting as important partners to CBH I in nature (Väljamäe *et al.*, 2001). Such protein yields are comparable or exceed the respective parameters for the best *Trichoderma sp.* strains (35–40 g/L) (Gusakov *et al.*, 2006). Yeast and fungi tolerate a range of 3.5 to 5.0 pH. The ability to lower pH below 4.0 offers a method for present operators using yeast in less than aseptic equipment to minimize loss due to bacterial contaminants.

Fungal lignocellulolytic enzymes for conversion of lignocellulosic biomass to fermentable sugars for the production of bioethanol were used (Tabka *et al.*, 2006). Wheat straw was pretreated by acid treatment with diluted sulfuric acid followed by steam explosion. Several enzymatic treatments implementing hydrolases (cellulases and xylanases from *Trichoderma reesei*, recombinant feruloyl esterase (FAE) from *Aspergillus niger* and oxidoreductases (laccases from

Pycnoporus cinnabarinus) were investigated to the saccharification of exploded wheat straw. A synergistic effect between cellulases, FAE and xylanase was proven under a critical enzymatic concentration (10 U/g of cellulases, 3 U/g of xylanase and 10 U/g of FAE). The yield of enzymatic hydrolysis was enhanced by increasing the temperature from 310 K to 323 K and addition of a non-ionic surfactant, Tween 20 (Tabka *et al.*, 2006).

4.3.5 Bioethanol Feedstocks

Biological feedstocks that contain appreciable amounts of sugar – or materials that can be converted into sugar, such as starch or cellulose – can be fermented to produce ethanol to be used in gasoline engines. Ethanol feedstocks can be conveniently classified into three types: (1) sucrose-containing feedstocks, (2) starchy materials, and (3) lignocellulosic biomass.

Today the production cost of bioethanol from lignocellulosic materials is still too high, which is the major reason why bioethanol has not made its breakthrough yet. When producing bioethanol from maize or sugar cane the raw material constitutes about 40–70% of the production cost.

Feedstock for bioethanol is essentially comprised of sugar cane and sugar beet. The two are produced in geographically distinct regions. Sugar cane is grown in tropical and subtropical countries, while sugar beet is only grown in temperate climate countries.

The conversion of sucrose into ethanol is easier compared to starchy materials and lignocellulosic biomass because previous hydrolysis of the feedstock is not required since this disaccharide can be broken down by the yeast cells; in addition, the conditioning of the cane juice or molasses favors the hydrolysis of sucrose.

Another type of feedstock, which can be used for bioethanol production, is starch-based materials. Starch is a biopolymer and defines as a homopolymer consisting of only one monomer, D-glucose. To produce bioethanol from starch it is necessary to break down the chains of this carbohydrate to obtain glucose syrup, which can be converted into ethanol by yeasts. The single greatest cost in the production of bioethanol from corn, and the cost with the greatest variability, is the cost of the corn.

Lignocellulosic biomass, such as agricultural residues (corn stover and wheat straw), wood and energy crops, is attractive materials for ethanol fuel production since it is the most abundant reproducible resources on Earth. Lignocellulosic perennial crops (*e.g.*, short rotation coppices and grasses) are promising feedstock because of high yields, low costs, good suitability for low quality land (which is more easily available for energy crops), and low environmental impacts.

Cellulosic biomass is a complex mixture of carbohydrate polymers from plant cell walls known as cellulose and hemicelluloses. The structural composition of various types of cellulosic biomass materials are given in Table 4.5. A cellulosic biomass differs from corn kernels for the methanol conversion process. Corn kernel is easier to process into ethanol than is cellulosic biomass. However, cellulosic

Table 4.5 Composition of various types of cellulosic biomass materials (% dry weight)

Material	Cellulose	Hemicelluloses	Lignin	Ash	Extractives
Algae (green)	20–40	20–50	–	–	–
Grasses	25–40	25–50	10–30	–	–
Hardwoods	45±2	30±5	20±4	0.6±0.2	5±3
Softwoods	42±2	27±2	28±3	0.5±0.1	3±2
Cornstalks	39–47	26–31	3–5	12–16	1–3
Wheat straw	37–41	27–32	13–15	11–14	7±2
Newspapers	40–55	25–40	18–30	–	–
Chemical pulps	60–80	20–30	2–10	–	–

Source: Demirbas, 2005b

Table 4.6 Relative abundance of individual sugars in carbohydrate fraction of wood (% by weight)

Sugar	In softwoods	In hardwoods
Glucose	61–65	55–73
Xylose	9–13	20–39
Mannose	7–16	0.4–4
Galactose	6–17	1–4
Arabinose	<3.5	<1

biomass is less expensive to produce than corn kernels by a factor of roughly 2 on a *per* ton basis, and the amount of ethanol that can be produced *per* acre of land of a given quality is higher for cellulosic biomass than for corn kernels. Relative to corn kernel, production of a perennial cellulosic biomass crop such as switchgrass requires lower inputs of energy, fertilizer, pesticide, and herbicide, and is accompanied by less erosion and improved soil fertility.

Cellulose molecules consist of long chains of glucose molecules (6-carbon sugars) as do starch molecules, but they have a different structural configuration. These structural characteristics plus the encapsulation by lignin makes cellulosic materials more difficult to hydrolyze than starchy materials. Hemicelluloses are also comprised of long chains of sugar molecules; but contain pentoses, in addition to glucose. The relative abundance of individual sugars in carbohydrate fraction of wood is shown in Table 4.6.

4.3.6 Fuel Properties of Ethanol

Ethanol is a liquid biofuel which can be produced from several different biomass feedstocks and conversion technologies. Bioethanol is an attractive alternative fuel because it is a renewable bio-based resource and it is oxygenated, thereby providing the potential to reduce particulate emissions in compression-ignition engines.

Ethanol can be made synthetically from petroleum or by microbial conversion of biomass materials through fermentation. In 1995, about 93% of the ethanol in the world was produced by the fermentation method and about 7% by the synthetic method. The fermentation method generally uses three steps: (1) the formation of a solution of fermentable sugars, (2) the fermentation of these sugars to ethanol, and (3) the separation and purification of the ethanol, usually by distillation.

Ethanol, unlike gasoline, is an oxygenated fuel that contains 35% oxygen, which reduces particulate and NO_x emissions from combustion. Ethanol is produced a more environmentally benign fuel. The systematic effect of ethyl alcohol differs from that of methyl alcohol. Ethyl alcohol is rapidly oxidized in the body to carbon dioxide and water, and in contrast to methyl alcohol no cumulative effect occurs. Ethanol is also a preferred alcohol in the transesterification process compared to methanol because it is derived from agricultural products and is renewable and biologically less objectionable in the environment.

Bioethanol has a higher octane number, broader flammability limits, higher flame speeds, and higher heats of vaporization than gasoline. These properties allow for a higher compression ratio, shorter burn time, and leaner burn engine, which leads to theoretical efficiency advantages over gasoline in an internal combustion engine. Disadvantages of bioethanol include its lower energy density than gasoline (but about 35% higher than that of methanol), its corrosiveness, low flame luminosity, lower vapor pressure (making cold starts difficult), miscibility with water, and toxicity to ecosystems.

Because bioethanol contains oxygen (35% of oxygen content) in the fuel, it can effectively reduce particulate matter emission in the diesel engine. Bioethanol is appropriate for the mixed fuel in the gasoline engine because of its high octane number, and its low cetane number and high heat of vaporization impede self-ignition in the diesel engine. The most popular blend for light-duty vehicles is known as E85, and contains 85% bioethanol and 15% gasoline. In Brazil, bioethanol for fuel is derived from sugarcane and is used pure or blended with gasoline in a mixture called gasohol (24% bioethanol, 76% gasoline). In several states of the United States, a small amount of bioethanol (10% by vol.) is added to gasoline, known as gasohol or E10. Blends having higher concentrations of bioethanol in gasoline are also used, *e.g.*, in flexible-fuel vehicles that can operate on blends of up to 85% bioethanol – E85. Some countries have exercised a biofuel program form the bioethanol-gasoline blend program, for example, the United States (E10 and for Flexible Fuel Vehicle (FFV) E85), Canada (E10 and for FFV E85), Sweden (E5 and for FFV E85), India (E5), Australia (E10), Thailand (E10), China (E10), Columbia (E10), Peru (E10), Paraguay (E7), and Brazil (E20, E25 and FFV any blend) (Kadiman, 2005).

As biomass hydrolysis and sugar fermentation technologies approach commercial viability, advancements in product recovery technologies will be required. For cases in which fermentation products are more volatile than water, recovery by distillation is often the technology of choice. Distillation technologies that allow the economic recovery of dilute volatile products from streams containing a vari-

ety of impurities have been developed and commercially demonstrated. A distillation system separates the bioethanol from water in the liquid mixture.

The first step is to recover the bioethanol in a distillation or beer column, where most of the water remains with the solids part. The product (37% bioethanol) is then concentrated in a rectifying column to a concentration just below the azeotrope (95%). The remaining bottoms product is fed to the stripping column to remove additional water, with the bioethanol distillate from stripping being recombined with the feed to the rectifier. The recovery of bioethanol in the distillation columns in the plant is fixed to be 99.6% to reduce bioethanol losses.

After the first effect, solids are separated using a centrifuge and dried in a rotary dryer. A portion (25%) of the centrifuge effluent is recycled to fermentation and the rest is sent to the second and third evaporator effects. Most of the evaporator condensate is returned to the process as fairly clean condensate (a small portion, 10%, is split off to waste water treatment to prevent build-up of low-boiling compounds) and the concentrated syrup contains 15–20% by weight total solids (Balat *et al.*, 2008).

4.4 Biomethanol

Methanol (CH_3OH or MeOH) is also known as “wood alcohol”. Generally, methanol is easier to find than ethanol. Sustainable methods of methanol production are currently not economically viable. Methanol is produced from synthetic gas or biogas and evaluated as a fuel for internal combustion engines. The production of methanol is a cost intensive chemical process. Therefore, in current conditions, only waste biomass such as old wood or biowaste is used to produce methanol (Vasudevan *et al.*, 2005).

The use of methanol as a motor fuel received attention during the oil crises of the 1970s due to its availability and low cost. Problems occurred early in the development of gasoline-methanol blends. As a result of its low price some gasoline marketers over blended. Many tests have shown promising results using 85–100% by volume methanol as a transportation fuel in automobiles, trucks, and buses.

Methanol can be used as one possible replacement for conventional motor fuels. Methanol has been seen as a possible large volume motor fuel substitute at various times during gasoline shortages. It was often used in the early part of 20th century to power automobiles before inexpensive gasoline was widely introduced. In the early 1920s, some viewed it as a source of fuel before new techniques were developed to discover and extract oil. Synthetically produced methanol was widely used as a motor fuel in Germany during the World War.

Before modern production technologies were developed in the 1920s, methanol was obtained from wood as a co-product of charcoal production and, for this reason, was commonly known as wood alcohol. However, the yield from this method of production was very low. One ton of hardwood yielded only 1% or 2% methanol. This led to its eventual replacement by less expensive alternatives. Biomass

resources can be used to produce methanol. The pyroligneous acid obtained from wood pyrolysis consists of about 50% methanol, acetone, phenols, and water. Biomass resources include crop residues, forage, grass, crops, wood resources, forest residues, short-rotation wood energy crops, and the lignocellulosic components of municipal solid waste. As a renewable resource, biomass represents a potentially inexhaustible supply of feedstock for methanol production. The product yield for the conversion process is estimated to be 185 kg of methanol *per* metric ton of solid waste. Methanol is currently made from natural gas but can be made using wood waste or garbage *via* partial oxidation reaction into syngas, followed by catalytic conversion into methanol called biomethanol. Adding sufficient hydrogen to the syngas to convert all of the biomass carbon into methanol carbon would more than double the methanol produced from the same biomass base. Current natural gas feedstocks are so inexpensive that even with tax incentives renewable methanol has not been able to compete economically. Technologies are being developed that may eventually result in commercial viability of renewable methanol.

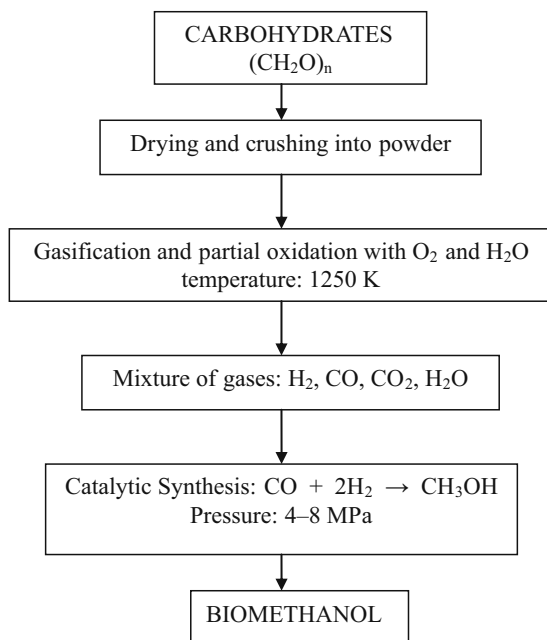
Biomass and coal can be considered as a potential fuel for gasification and further syngas production and methanol synthesis. The feasibility of achieving the conversion has been demonstrated in a large scale system in which a product gas is initially produced by pyrolysis and gasification of a carbonaceous matter. The synthetic process developed in 1927 replaced this traditional method. Methanol from biochar was about 1–2% of volume or 6 gallons *per* ton. Syngas from biomass is altered by catalyst under high pressure and temperature to form methanol. This method will produce 100 gallons of methanol *per* ton of feed material. Figure 4.5 shows biomethanol obtained from carbohydrates by gasification and partial oxidation with O_2 and H_2O .

Methanol is poisonous and burns with an invisible flame. Just like ethyl alcohol methanol has a high octane rating and hence an Otto engine is preferable. Most processes require supplemental oxygen for the intermediate conversion of the biomass into a synthesis gas ($H_2 + CO$). A readily available supply of hydrogen and oxygen, therefore, should improve the overall productivity of biomass derived methanol (Ouellette *et al.*, 1997).

Before modern production technologies were developed in the 1920s, methanol was obtained from wood as a co-product of charcoal production and, for this reason, was commonly known as wood alcohol. Methanol is currently manufactured worldwide by conversion or derived from syngas, natural gas, refinery off-gas, coal or petroleum ($2H_2 + CO \rightarrow CH_3OH$). The chemical composition of syngas from coal and then from natural gas can be identical with the same H_2/CO ratio. A variety of catalysts are capable of causing the conversion, including reduced NiO-based preparations, reduced Cu/ZnO shift preparations, Cu/SiO₂ and Pd/SiO₂, and Pd/ZnO (Takezawa *et al.*, 1987; Iwasa *et al.*, 1993).

Methanol is currently made from natural gas but can also be made using biomass *via* partial oxidation reactions (Demirbas and Güllü, 1998). Biomass and coal can be considered as a potential fuel for gasification and further syngas production and methanol synthesis (Takezawa *et al.*, 1987). Adding sufficient hydrogen to the synthesis gas to convert all of the biomass into methanol carbon then

Fig. 4.5 Biomethanol from carbohydrates by gasification and partial oxidation with oxygen and water
Source: Demirbas, 2008b



double the methanol produced from the same biomass base (Phillips *et al.*, 1990). Waste material can be partially converted to methanol, for which the product yield for the conversion process is estimated to be 185 kg of methanol *per* metric ton of solid waste (Brown *et al.*, 1952; Sorensen, 1983). Agriculture-(m)ethanol is at present more expensive than synthesis-ethanol from ethylene and of methanol from natural gas (Grassi, 1999).

Biomass resources can be used to produce methanol. The pyroligneous acid obtained from wood pyrolysis consists of about 50% methanol, acetone, phenols, and water (Demirbas and Güllü, 1998; Güllü and Demirbas, 2001). As a renewable resource, biomass represents a potentially inexhaustible supply of feedstock for methanol production. The composition of biosyngas from biomass for producing methanol is presented in Table 4.7. Current natural gas feedstocks are so inexpensive that even with tax incentives renewable methanol has not been able to compete economically. Technologies are being developed that may eventually result in the commercial viability of renewable methanol.

Methanol from coal may be a very important source of liquid fuel in the future. The coal is first pulverized and cleaned, then fed to a gasifier bed where it is reacted with oxygen and steam to produce syngas. Once these steps have been taken, the production process is much the same as with the other feedstocks with some variations in the catalyst used and the design of the converter vessel in which the reaction is carried out. Methanol is made using synthesis gas (syngas) with hydrogen and carbon monoxide in a 2:1 ratio (Table 4.7). The syngas is transformed to methanol in a fixed catalyst bed reactor. Coal-derived methanol has many preferable properties

Table 4.7 Composition of biosyngas from biomass gasification

Constituents	% by volume (dry and nitrogen free)
Carbon monoxide (CO)	28–36
Hydrogen (H ₂)	22–32
Carbon dioxide (CO ₂)	21–30
Methane (CH ₄)	8–11
Ethene (C ₂ H ₄)	2–4

such as being free of sulfur and other impurities, and may replace petroleum in transportation, or be used as a peaking fuel in combustion turbines, or supply a source of hydrogen for fuel cells. The technology for making methanol from natural gas is already in place and requires only efficiency improvements and scale-up to make methanol an economically viable alternative transportation fuel (Demirbas, 2000).

In recent years, a growing interest has been observed in the application of methanol as an alternative liquid fuel, which can be used directly for powering Otto engines or fuel cells (Chmielniak and Sciazko, 2003). The feasibility of achieving the conversion has been demonstrated in a large scale system in which a product gas is initially produced by pyrolysis and gasification of a carbonaceous matter. Syngas from biomass is altered by a catalyst under high pressure and temperature to form methanol. This method produces 100 gallons of methanol *per* ton of feed material (Rowell and Hokanson, 1979).

The gases produced can be steam reformed to produce hydrogen and followed by a water–gas shift reaction to further enhance hydrogen production. When the moisture content of biomass is higher than 35%, it can be gasified in a supercritical water condition (Hao and Guo, 2002). Supercritical water gasification is a promising process to gasify biomass with high moisture contents due to the high gasification ratio (100% achievable) and high hydrogen volumetric ratio (50% achievable) (Yoshida *et al.*, 2004; Matsumura and Minowa, 2004). Hydrogen produced by biomass gasification has been reported to be comparable to that by natural gas reforming (Bowen *et al.*, 2003). The process is more advantageous than fossil fuel reforming in consideration of environmental benefits. It is expected that biomass thermochemical conversion will become one of the most economical large-scale renewable hydrogen technologies.

The strategy is based on producing hydrogen from biomass pyrolysis using a co-product strategy to reduce the cost of hydrogen and it has been concluded that only this strategy may compete with the cost of the commercial hydrocarbon-based technologies (Wang *et al.*, 1998). This strategy will demonstrate how hydrogen and biofuel are economically feasible and can foster the development of rural areas when practiced on a larger scale. The process of biomass to activated carbon is an alternative route to hydrogen with a valuable co-product that is practiced commercially (Demirbas, 1998).

The simultaneous production of bio-methanol (obtained by the hydrogenation of CO₂ developed during the fermentation of sugar juice), in parallel to the production of bio-ethanol, appears to be economically attractive in locations where

Table 4.8 Main production facilities of methanol and biomethanol

Methanol	Biomethanol
Catalytic synthesis from CO and H ₂	Catalytic synthesis from CO and H ₂
Natural gas	Distillation of liquid from wood pyrolysis
Petroleum gas	Gaseous products from biomass gasification
Distillation of liquid from coal pyrolysis	Synthetic gas from biomass and coal

hydroelectricity is available at very low cost (~0.01 \$ Kwh) and where lignocellulosic residues are available as surpluses.

The gas is converted to methanol in a conventional steam-reforming/water–gas shift reaction followed by high-pressure catalytic methanol synthesis:



Equations 4.12 and 4.13 are called as gasification/shift reactions.



or



Equations 4.14 or 4.15 are methanol synthesis reactions.

The energy value of residues generated worldwide in agriculture and the forest products industry amounts to more than one-third of the total commercial primary energy used at present (Hall *et al.*, 1993). Bioenergy supplies can be divided into two broad categories: (a) organic municipal waste and residues from the food and materials sectors, and (b) dedicated energy crops plantations. Bioenergy from biomass, both residues and energy crops, can be converted into modern energy carriers such as hydrogen, methanol, ethanol, or electricity (Azar *et al.*, 2003).

Methanol can be produced from biomass essentially any primary energy source. Thus, the choice of fuel in the transportation sector is to some extent determined by the availability of biomass. As regards the difference between hydrogen and methanol production costs, conversion of natural gas, biomass, and coal into hydrogen is generally more energy efficient and less expensive than conversion into methanol (Azar *et al.*, 2003). The main production facilities of methanol and biomethanol are given in Table 4.8.

4.5 Vegetable Oils

Vegetable oils and animal fats are chemically triglyceride molecules in which the three fatty acids groups are esters attached to one glycerol molecule (Gunstone and Hamilton, 2001). Fats and oils are primarily water-insoluble, hydrophobic

substances in the plant and animal kingdom that are made up of one mole of glycerol and three moles of fatty acids and are commonly referred to as triglycerides (Sonntag, 1979). Triglycerides are esters of glycerin with different carboxylic acids. The triglyceride molecules differ by the nature of the alkyl chain bound to glycerol. The proportions of the various acids vary from fat to fat; each fat has its characteristic composition. Although thought of as esters of glycerin and a varying blend of fatty acids, these oils in fact contain free fatty acids and diglycerides as well. Triglyceride vegetable oils and fats include not only edible, but also inedible vegetable oils and fats such as linseed oil, castor oil, and tung oil, used in lubricants, paints, cosmetics, pharmaceuticals, and for other industrial purposes. Some physical properties of the most common fatty acids occurring in vegetable oils and animal fats as well as their methyl esters are listed in Tables 4.9 and 4.10.

Vegetable oils have become more attractive recently because of their environmental benefits and the fact that they are made from renewable resources. More than 100 years ago, Rudolf Diesel tested vegetable oil as the fuel for his engine (Shay, 1993). Vegetable oils have the potential to substitute for a fraction of the petroleum distillates and petroleum-based petrochemicals in the near future. Vegetable oil fuels are not yet petroleum competitive fuels because they are more expensive than petroleum fuels. However, with the recent increases in petroleum prices and the uncertainties concerning petroleum availability, there is renewed interest in using vegetable oils in diesel engines (Giannelos *et al.*, 2002).

Table 4.9 Selected properties of some common fatty acids in vegetable oils and animal fats

Common name (systematic name)	Carbon number: double bond number	Molecular weight	Melting point (K)
Caprylic acid (octanoic acid)	8:0	144.22	289.7
Capric acid (decanoic acid)	10:0	172.27	304.7
Lauric acid (dodecanoic acid)	12:0	200.32	317.2
Myristic acid (tetradecanoic acid)	14:0	228.38	331.2
Palmitic acid (hexadecanoic acid)	16:0	256.43	336.2
Stearic acid (octadecanoic acid)	18:0	284.48	344.2
Oleic acid (9Z-octadecenoic acid)	18:1	282.47	289.2
Linoleic acid (9Z,12Z-octadecadienoic acid)	18:2	280.45	268.2
Linolenic acid (9Z,12Z,15Z-octadecatrienoic acid)	18:3	278.44	262.2
Erucic acid (13Z-docosenoic acid)	22:1	338.58	305–307

Table 4.10 Selected properties of some common fatty acid methyl esters

Common name (systematic name)	Carbon number: double bond number	Molecular weight	Melting point (K)	Cetane number
Methyl caprylate (methyl octanoate)	8:0	158.24	—	33.6
Methyl caprate (methyl decanoate)	10:0	186.30	—	47.7
Methyl laurate (methyl dodecanoate)	12:0	214.35	278.2	61.4
Methyl myristate (methyl tetradecanoate)	14:0	242.41	291.7	66.2
Methyl palmitate (methyl hexadecanoate)	16:0	270.46	303.7	74.5
Methyl stearate (methyl octadecanoate)	18:0	298.51	312.3	86.9
Methyl oleate (methyl 9Zocta- decanoate)	18:1	296.49	253.2	47.2
Methyl linoleate (methyl 9Z, 12Z—octadecadienoate)	18:2	294.48	238.2	28.5
Methyl linolenate (methyl 9Z, 12Z, 15Z—octadecatrienoate)	18:3	292.46	216.2	20.6
Methyl erucate (methyl 13Zdocosenoate)	22:1	352.60	—	76.0

Vegetable oils and fats are substances derived from plants that are composed of triglycerides. Oils extracted from plants have been used in many cultures since ancient times. The oily seed and nut kernels contain 20–60% oil. Fatty acid compositions of vegetable oils and fats are listed in Table 4.11.

As can be seen from Table 4.11, palmitic (16:0) and stearic (18:0) are two most common saturated fatty acids, with every vegetable oil containing at least a small amount of each one. Similarly, oleic (18:1) and linoleic (18:2) are the most common unsaturated fatty acids. Many of the oils also contain some linolenic acid (18:3).

Today, the world's largest producer of soybeans is the US with the majority of cultivation located in the midwest and south. Soybeans must be carefully cleaned, dried, and dehulled prior to oil extraction. There are three main methods for extracting oil from soybeans. These procedures are hydraulic pressing, expeller pressing, and solvent extraction.

There are more than 350 oil-bearing crops identified, among which only soybean, palm, sunflower, safflower, cottonseed, rapeseed, and peanut oils are considered as potential alternative fuels for diesel engines (Goering *et al.*, 1982; Pryor *et al.*, 1982). Table 4.12 shows the oil species that can be used in biodiesel production. Worldwide consumption of soybean oil is the highest in 2003 (27.9 million

Table 4.11 Fatty acid compositions of vegetable oils and fats*

Sample	16:0	16:1	18:0	18:1	18:2	18:3	Others
Cottonseed	28.7	0	0.9	13.0	57.4	0	0
Poppyseed	12.6	0.1	4.0	22.3	60.2	0.5	0
Rapeseed	3.8	0	2.0	62.2	22.0	9.0	0
Safflower seed	7.3	0	1.9	13.6	77.2	0	0
Sunflower seed	6.4	0.1	2.9	17.7	72.9	0	0
Sesame seed	13.1	0	3.9	52.8	30.2	0	0
Linseed	5.1	0.3	2.5	18.9	18.1	55.1	0
Wheat grain ^a	20.6	1.0	1.1	16.6	56.0	2.9	1.8
Palm	42.6	0.3	4.4	40.5	10.1	0.2	1.1
Corn marrow	11.8	0	2.0	24.8	61.3	0	0.3
Castor ^b	1.1	0	3.1	4.9	1.3	0	89.6
Tallow	23.3	0.1	19.3	42.4	2.9	0.9	2.9
Soybean	11.9	0.3	4.1	23.2	54.2	6.3	0
Bay laurel leaf ^c	25.9	0.3	3.1	10.8	11.3	17.6	31.0
Peanut kernel ^d	11.4	0	2.4	48.3	32.0	0.9	4.0
Hazelnut kernel	4.9	0.2	2.6	83.6	8.5	0.2	0
Walnut kernel	7.2	0.2	1.9	18.5	56.0	16.2	0
Almond kernel	6.5	0.5	1.4	70.7	20.0	0	0.9
Olive kernel	5.0	0.3	1.6	74.7	17.6	0	0.8
Coconut ^e	7.8	0.1	3.0	4.4	0.8	0	65.7

*xx:y: xx number of carbon atoms; y number of double bonds.

^aWheat grain oil contains 11.4% of 8:0 and 0.4% of 14:0 fatty acids.

^bCastor oil contains 89.6% ricinoleic acid.

^cBay laurel oil contains 26.5% of 12:0 and 4.5% of 14:0 fatty acids.

^dPeanut kernel oil contains about 2.7% of 22:0 and 1.3% of 24:0 fatty acids.

^eCoconut oil contains about 8.9% of 8:0, 6.2% 10:0, 48.8% of 12:0 and 19.9% of 14:0 fatty acids.

Table 4.12 Oil species for biofuel production

Group	Source of oil
Major oils	Coconut (copra), corn (maize), cottonseed, canola (a variety of rapeseed), olive, peanut (ground nut), safflower, sesame, soybean, sunflower
Nut oils	Almond, cashew, hazelnut, macadamia, pecan, pistachio, walnut
Other edible oils	Amaranth, apricot, argan, artichoke, avocado, babassu, bay laurel, beech nut, ben, Borneo tallow nut, carob pod (algaroba), cohune, coriander seed, false flax, grape seed, hemp, kapok seed, lallemantia, lemon seed, macauba fruit (<i>Acrocomia sclerocarpa</i>), meadowfoam seed, mustard, okra seed (hibiscus seed), perilla seed, pine nut, poppyseed, prune kernel, quinoa, ramtil, niger pea), rice bran, tallow, tea (camellia), thistle seed, and wheat germ
Inedible oils	Algae, babassu tree, copaiba, honge, jatropha or ratanjyote, jojoba, karanja or honge, mahua, milk bush, nagchampa, neem, petroleum nut, rubber seed tree, silk cotton tree, tall
Other oils	Castor, radish, tung

Table 4.13 World vegetable and marine oil consumption (million metric tons)

Oil	1998	1999	2000	2001	2002	2003
Soybean	23.5	24.5	26.0	26.6	27.2	27.9
Palm	18.5	21.2	23.5	24.8	26.3	27.8
Rapeseed	12.5	13.3	13.1	12.8	12.5	12.1
Sunflower seed	9.2	9.5	8.6	8.4	8.2	8.0
Peanut	4.5	4.3	4.2	4.7	5.3	5.8
Cottonseed	3.7	3.7	3.6	4.0	4.4	4.9
Coconut	3.2	3.2	3.3	3.5	3.7	3.9
Palm kernel	2.3	2.6	2.7	3.1	3.5	3.7
Olive	2.2	2.4	2.5	2.6	2.7	2.8
Fish	1.2	1.2	1.2	1.3	1.3	1.4
Total	80.7	85.7	88.4	91.8	95.1	98.3

metric tons). Table 4.13 shows the world vegetable and marine oil consumption between 1998 and 2003.

Vegetable oil is a biorenewable fuel and is a potentially inexhaustible source of energy having an energy content close to diesel fuel. On the other hand, extensive use of vegetable oils may cause other significant problems such as starvation in developing countries. Vegetable oil fuels have not been acceptable because they are more expensive than petroleum fuels. However, with recent increases in petroleum prices and uncertainties concerning petroleum availability, there is renewed interest in vegetable oil fuels for diesel engines (Demirbas, 2003b; Giannelos *et al.*, 2002).

The first use of vegetable oils as a fuel was in 1900. Vegetable oils have become more attractive recently because of their environmental benefits and the fact that they are made from renewable resources. The advantages of vegetable oils as diesel fuel are liquidity, ready availability, renewability, lower sulfur and aromatic content, and biodegradability (Goering *et al.*, 1982). The main disadvantages of vegetable oils as diesel fuel are higher viscosity, lower volatility, and the reactivity of unsaturated hydrocarbon chains. The problems met in long-term engine tests, according to results obtained by earlier researchers (Komers *et al.*, 2001; Darnoko and Cheryan, 2000) may be classified as follows: injector coking on the injectors, more carbon deposits, oil ring sticking and thickening, and gelling of the engine lubricant oil. Vegetable oils were all extremely viscous, with viscosities 8–15 times greater than No. 2 diesel fuel (No. 2 diesel fuel is a diesel engine fuel with 10–20 carbon number hydrocarbons) (Srivastava and Prasad, 2000).

A variety of biolipids can be used to produce biodiesel. These are: (a) virgin vegetable oil feedstock; rapeseed and soybean oils are most commonly used, though other crops such as mustard, palm oil, sunflower, hemp and even algae show promise; (b) waste vegetable oil; (c) animal fats including tallow, lard, and yellow grease; and (d) non-edible oils such as jatropha oil, neem oil, mahua oil, castor oil, tall oil, *etc.*

Soybeans are common use in the United States for food products this has led to soybean biodiesel becoming the primary source for biodiesel in that country. In

Malaysia and Indonesia palm oil is used as a significant biodiesel source. In Europe, rapeseed is the most common base oil used in biodiesel production. In India and Southeast Asia, the jatropha tree is used as a significant fuel source.

Algae can grow practically in every place where there is enough sunshine. Some algae can grow in saline water. The most significant different of algal oil is in the yield and hence its biodiesel yield. According to some estimates, the yield (*per* acre) of oil from algae is over 200 times the yield from the best-performing plant/vegetable oils (Sheehan *et al.*, 1998). Microalgae are the fastest growing photosynthesizing organisms. They can complete an entire growing cycle every few days. Approximately 46 tons of oil/hectare/year can be produced from diatom algae. Different algae species produce different amounts of oil. Some algae produce up to 50% oil by weight. The production of algae to harvest oil for biodiesel has not been undertaken on a commercial scale, but working feasibility studies have been conducted to arrive at the above number.

4.5.1 Alternatives to Diesel Fuel

The diesel engine is used mainly for heavy vehicles. Diesel fuel consists of hydrocarbons with between 9 and 27 carbon atoms in a chain as well as a smaller amount of sulfur, nitrogen, oxygen, and metal compounds. It is a general property of hydrocarbons that the auto-ignition temperature is higher for more volatile hydrocarbons. The hydrocarbons present in the diesel fuels include alkanes, naphthenes, olefins, and aromatics.

The main advantage of the diesel engine is that the level of efficiency is greater than in the Otto cycle engine. This means that a greater part of the energy content of the fuel is exploited. The efficiency of a diesel engine is at best 45%, compared with 30% for the Otto engine.

Diesel emissions contain low concentrations of carbon monoxide and hydrocarbons. The major problem with diesel emissions are nitric oxides and particles, as these are the most difficult to reduce.

Alternate fuels for diesel engines or heavy-duty vehicles (HDVs) contain Fischer–Tropsch (F–T) diesel, dimethyl ether (DME), vegetable oil, and biodiesel. Both F–T and DME can be manufactured from natural gas and are therefore not limited by feedstock availability. Biodiesel on the other hand, is produced from vegetable oils whose supply for non-nutritional uses is presently quite limited.

Dimethyl ether (DME or $\text{CH}_3\text{-O-CH}_3$) is a new fuel which has attracted much attention recently. Today DME is made from natural gas, but DME can also be produced by gasifying biomass. DME can be stored in liquid form at 5–10 bar pressure at normal temperature. A major advantage of DME is its naturally high cetane number, which means that self-ignition is easier. The high cetane rating makes DME most suitable for use in diesel engines, which implies that the high level of efficiency of the diesel engine is retained when using DME. The energy content of DME is lower than in diesel.

DME can be produced effectively from syngas in a single-stage, liquid phase (LPDME) process. The origin of syngas includes a wide spectrum of feedstocks such as coal, natural gas, biomass, and others. Non-toxic, high density, liquid DME fuel can be easily stored at modest pressures. The production of DME is very similar to that of methanol. DME conversion to hydrocarbons, lower olefins in particular, is studied using ZSM-5 catalysts with varying $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios, whereas the DME carbonization reaction to produce methyl acetate is studied over a variety of group VIII metal substituted heteropolyacid catalysts.

The single-stage, LPDME process is very significant from both scientific and commercial perspectives. DME can be effectively converted to gasoline-range hydrocarbons, lower olefins, and other oxygenates. It may be used directly as a transportation fuel in admixtures with methanol or as a fuel additive. In particular, dimethyl ether is shaping up as an ultra-clean alternative fuel for diesel engines. The advantages of using DME are ultra-low emissions of nitrogen oxides (NO_x), reduced engine noise or quiet combustion, practically soot-free or smokeless operation and hence no exhaust after treatment, and high diesel thermal efficiency.

A sustainable biofuel has two favorable properties which are availability from renewable raw material and its lower negative environmental impact compared to fossil fuels. As an alternative fuel vegetable oil is one of the renewable fuels. Vegetable oil is a potentially inexhaustible source of energy with an energetic content close to diesel fuel.

Vegetable oils, such as palm, soybean, sunflower, peanut, and olive oils as alternative fuels can be used for diesel engines. Due to the rapid decline in crude oil reserves, the use of vegetable oils as diesel fuels is again being promoted in many countries. The effect of coconut oil as a diesel fuel alternative or as a direct fuel blend has been investigated using a single-cylinder, direct-injection diesel engine (Machacon *et al.*, 2001).

Vegetable oils have the potential to substitute a fraction of petroleum distillates and petroleum-based petrochemicals in the near future. Vegetable oil fuels are not petroleum-competitive fuels because they are more expensive than petroleum fuels. However, with recent increases in petroleum prices and uncertainties concerning petroleum availability, there is renewed interest in using vegetable oils in diesel engines.

Short term tests are showing promising results by using neat vegetable oil. Problems appear only after the engine has been operating on vegetable oil for longer periods of time. Problems met in long-term engine tests according to results obtained by earlier researchers may be classified as follows: injector coking and trumpet formation on the injectors, more carbon deposits, oil ring sticking, and thickening and gelling of the engine lubricant oil (Demirbas, 2003b).

Biodiesel is a fuel consisting of long-chain fatty acid alkyl esters made from renewable vegetable oils, recycled cooking greases, or animal fats. Vegetable oil (m)ethyl esters, commonly referred to as "biodiesel", are prominent candidates as alternate diesel fuels (Vicente *et al.*, 2004). Biodiesel is technically competitive with or offers technical advantages compared to conventional petroleum diesel fuel. Compared to No. 2 diesel fuel, all vegetable oils are much more viscous, while

Table 4.14 Fuel properties of methyl ester biodiesels

Source	Viscosity cSt at 313.2 K	Density g/mL at 288.7 K	Cetane number	References
Sunflower	4.6	0.880	49	(Pischinger <i>et al.</i> , 1982)
Soybean	4.1	0.884	46	(Schwab <i>et al.</i> , 1987)
Palm	5.7	0.880	62	(Nelson and Courter, 1954)
Peanut	4.9	0.876	54	(Srivastava and Prasad, 2000)
Babassu	3.6	—	63	(Srivastava and Prasad, 2000)
Tallow	4.1	0.877	58	(Ali <i>et al.</i> , 1995)

methyl esters of vegetable oils are the slightly more viscous. The methyl esters are more volatile than those of the vegetable oils. The soaps obtained from the vegetable oils can be pyrolyzed into hydrocarbon-rich products (Demirbas, 2002).

The properties of biodiesel are close to diesel fuels. The biodiesel was characterized by determining its viscosity, density, cetane number, cloud and pour points, characteristics of distillation, flash and combustion points, and higher heating value (HHV) according to ISO norms. Some fuel properties of methyl ester biodiesels are presented in Table 4.14.

The viscosity of the distillate was 10.2 mm²/s at 311 K, which is higher than the ASTM specification for No. 2 diesel fuel (1.9–4.1 mm²/s) but considerably below that of soybean oil (32.6 mm²/s). Used cottonseed oil from the cooking process was decomposed with Na₂CO₃ as catalyst at 725 K to give a pyrolyzate containing mainly C₈₋₂₀ alkanes (69.6%) besides alkenes and aromatics. The pyrolyzate had lower viscosity, pour point, and flash point than No. 2 diesel fuel and equivalent heating values. The cetane number of the pyrolyzate was lower than that of No. 2 diesel fuel (Bala, 2005).

Engine tests have demonstrated that methyl esters produce slightly higher power and torque than ethyl esters (Encinar *et al.*, 2002). The methyl ester of vegetable oil has been evaluated as a fuel in compression ignition engines (CIE) by researchers (Isigigur *et al.*, 1994; Kusdiana and Saka, 2001).

Biodiesel fuels have generally been found to be non-toxic and are biodegradable, which may promote their use in applications where biodegradability is desired. Neat biodiesel and biodiesel blends reduce particulate matter (PM), hydrocarbons (HC) and carbon monoxide (CO) emissions and increase nitrogen oxides (NO_x) emissions compared with petroleum-based diesel fuel used in an unmodified diesel engine (EPA, 2002).

4.5.2 Vegetable Oil Resources

World annual petroleum consumption and vegetable oil production is about 4.018 and 0.107 billion tons, respectively. Global vegetable oil production increased 56 million tons in 1990 to 88 million tons in 2000, following a below-normal in-

Table 4.15 World vegetable and marine oil consumption (million metric tons)

Oil	1998	1999	2000	2001	2002	2003
Soybean	23.5	24.5	26.0	26.6	27.2	27.9
Palm	18.5	21.2	23.5	24.8	26.3	27.8
Rapeseed	12.5	13.3	13.1	12.8	12.5	12.1
Sunflower seed	9.2	9.5	8.6	8.4	8.2	8.0
Peanut	4.5	4.3	4.2	4.7	5.3	5.8
Cottonseed	3.7	3.7	3.6	4.0	4.4	4.9
Coconut	3.2	3.2	3.3	3.5	3.7	3.9
Palm kernel	2.3	2.6	2.7	3.1	3.5	3.7
Olive	2.2	2.4	2.5	2.6	2.7	2.8
Fish	1.2	1.2	1.2	1.3	1.3	1.4
Total	80.7	85.7	88.4	91.8	95.1	98.3

crease. World vegetable and marine oil consumption is tabulated in Table 4.15. Figure 4.6 shows the plots of percentages the world oil consumption according to years. Leading the gains in vegetable oil production was a recovery in world palm oil output, from 18.5 million tons in 1998 to 27.8 million in 2003.

The major exporters of vegetable oils are Malaysia, Argentina, Indonesia, the Philippines, and Brazil. The major importers of vegetable oils are China, Pakistan, Italy, and the United Kingdom. A few countries such as the Netherlands, Germany, the United States, and Singapore are both large exporters as well as importers of vegetable oils (Bala, 2005).

Global vegetable oil consumptions rose modestly from 79.5 million tons in 1998 to 96.9 million in 2003. A large portion of the gain went to India, where even

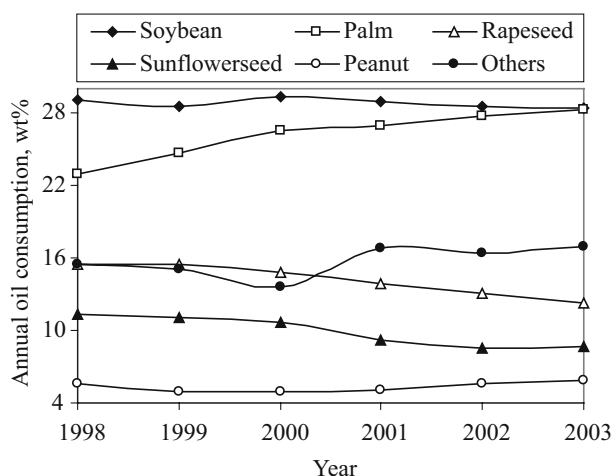
**Fig. 4.6** Plots of percentages of world oil consumption according to years

Table 4.16 Oils and fats feedstock distribution top ten developed economy countries with self-sufficiency potential in 2006

Feedstock	%
Animal fats	52
Soybean oil	20
Rapeseed oil	11
Palm oil	6
Sunflower oil	5
Other vegetable oils	5

small price shifts can cause a substantial change in consumption. Indian palm oil imports climbed to a record 2.5 million tons. Similarly, Pakistan, Iran, Egypt, and Bangladesh sharply increased their vegetable oil imports. In 1999, Pakistan reacted to falling vegetable oil prices with a series of increases that doubled the import duties on soybean oil and palm oil, while eliminating duties on oilseeds. Pakistan also raised the import duty on soybean meal from 10% to 35% to stem the influx of Indian exports (Erickson *et al.*, 1980).

Table 4.16 shows the oils and fats feedstock distribution top ten developed economy countries with self-sufficiency potential in 2006.

4.5.2.1 Inedible Oil Resources

The main commodity sources for biodiesel production from inedible oils can be obtained from plant species such as jatropha or ratanjyote or seemaikattamankku (*Jatropha curcas*), karanja or honge (*Pongamia pinnata*), nagchampa (*Calophyllum inophyllum*), rubber seed tree (*Hevea brasiliensis*), neem (*Azadirachta indica*), mahua (*Madhuca indica* and *Madhuca longifolia*), silk cotton tree (*Ceiba pentandra*), jojoba (*Simmondsia chinensis*), babassu tree, *Euphorbia tirucalli*, microalgae, *etc.* They are easily available in many parts of the world and are very cheap compared to edible oils in India. (Karmee and Chadha, 2005).

Two major species of the genus *Madhuca indica* and *Madhuca longifolia* are found in India. Oil of the rubber seed tree (*Hevea brasiliensis*) is a inedible source of biodiesel production. It is found mainly in Indonesia, Malaysia, Liberia, India, Srilanka, Sarawak, and Thailand. Rubber seed kernels (50–60% of seed) contain 40–50% of brown color oil (Ramadhas *et al.*, 2004). Two major species of the genus the oil palms, *Elaeis guineensis* and *Elaeis oleifera*, can be found in Africa and Central/South America, respectively. Among vegetable oils, the price of palm oil is the cheapest in palm-producing countries such as Malaysia, Indonesia, Thailand, and Korea. Neem oil is a vegetable oil pressed from the fruits and seeds of neem (*Azadirachta indica*), an evergreen tree that is endemic to the Indian subcontinent and has been introduced to many other areas native to India and Burma, growing in tropical and semitropical regions. Jojoba oil is produced in the seed of the jojoba (*Simmondsia chinensis*) plant, a shrub native to southern Arizona,

southern California and northwestern Mexico (Wikipedia, 2008). Oil of the silk cotton tree (*Ceiba pentandra*) is a inedible source of biodiesel production. The tree belongs to the *Bornbacacea* family. The silk cotton tree has great economic importance for both domestic and industrial uses in Nigeria. The seeds are also used as food/feed for humans and livestock in many part of the world such as India, Tanzania, and Mozambique. *Ceiba pentendra* crude oil was extracted for 24 hours using a Soxhlet extractor with n-hexane as a solvent (Das *et al.*, 2002). The babassu tree is a species of palm tree that is resource of light yellow clear oil. There are both edible and non-edible species of babassu oils. Non-edible species of the oil is obtained from the babassu tree that is widely grown in Brazil. Viscosity at 313.2 K and cetane number values of babassu oil are 3.6 cSt and 63, respectively (Srivastava and Prasad, 2000).

Fatty acid profiles of seed oils of 75 plant species having 30% or more fixed oil in their seed/kernel were examined and *Azadirachta indica*, *Calophyllum inophyllum*, *Jatropha curcas*, and *Pongamia pinnata* were found to be the most suitable for use as biodiesel (Shah *et al.*, 2005; Azam *et al.*, 2005). The seed oil of *Jatropha* was used as a diesel fuel substitute during World War II and as blends with diesel (Foidl *et al.*, 1996; Gubitz *et al.*, 1999; Shah *et al.*, 2004; Shah and Gupta, 2007). Thus *Jatropha curcas* and *Pongamia pinnata* (Karanja) are the most suitable for the purpose of production of renewable fuel as biodiesel (Meher *et al.*, 2006a; 2006b). *Jatropha* and Karanja have a high oil content (25–30%) (Foidl *et al.*, 1996; Shah *et al.*, 2004).

From 1978 to 1996, the US Department of Energy's Office of Fuels Development funded a program to develop renewable transportation fuels from algae (Sheehan *et al.*, 1998). Most current research on oil extraction is focused on microalgae to produce biodiesel from algal-oil. Algal-oil processes into biodiesel as easily as oil derived from land-based crops. The lipid and fatty acid contents of microalgae vary in accordance with culture conditions. All algae contain proteins, carbohydrates, lipids and nucleic acids in varying proportions. Algal-oil contains saturated and monounsaturated fatty acids. The fatty acids were determined in the algal oil in the following proportions: 36% oleic (18:1), 15% palmitic (16:0), 11% stearic (18:0), 8.4% iso-17:0, and 7.4% linoleic (18:2). The high proportion of saturated and monounsaturated fatty acids in this alga is considered optimal from a fuel quality standpoint, in that fuel polymerization during combustion would be substantially less than what would occur with polyunsaturated fatty acid-derived fuel (Sheehan *et al.*, 1998).

Algae can grow practically in every place where there is enough sunshine. Some algae can grow in saline water. The most significant different of algal oil is in the yield and hence its biodiesel yield. According to some estimates, the yield (*per acre*) of oil from algae is over 200 times the yield from the best-performing plant/vegetable oils (Sheehan *et al.*, 1998). Microalgae are the fastest growing photosynthesizing organisms. They can complete an entire growing cycle every few days. Approximately 46 tons of oil/hectare/year can be produced from diatom algae. Different algae species produce different amounts of oil. Some algae produce up to 50% oil by weight. Microalgae have much faster growth rates than

terrestrial crops. The *per* unit area yield of oil from algae is estimated to be from between 5,000 to 20,000 gallons *per* acre, *per* year; this is 7 to 31 times greater than the next best crop, palm oil.

4.5.3 *The Use of Vegetable Oils as Diesel Fuel*

The first engine like diesel engine was developed in the 1800s for fossil fuels. The famous German inventor Rudolf Diesel designed the original diesel engine to run on vegetable oil. Dr. Rudolf Diesel used peanut oil to fuel one of his engines at the Paris Exposition of 1900 (Nitschke and Wilson, 1965). Because of the high temperatures created, the engine was able to run a variety of vegetable oils including hemp and peanut oil. Life for the diesel engine began in 1893 when the Dr. Diesel published a paper entitled "The theory and construction of a rational heat engine". At the 1911 World Fair in Paris, Dr. Diesel ran his engine on peanut oil and declared that "the diesel engine can be fed with vegetable oils and will help considerably in the development of the agriculture of the countries which use it". One of the first uses of transesterified vegetable oil (biodiesel) was to power heavy-duty vehicles in South Africa before World War II.

The first International Conference on Plant and Vegetable Oils as fuels was held in Fargo, North Dakota in August 1982. The primary concerns discussed were the cost of the fuel, the effects of vegetable oil fuels on engine performance, durability and fuel preparation, specifications and additives (Ma and Hanna, 1999). Oil production, oilseed processing and extraction also were considered at this meeting (ASAE, 1982).

Diesel fuel can also be replaced by biodiesel made from vegetable oils. Biodiesel is now mainly being produced from soybean and rapeseed oils. Soybean oil is of primary interest as biodiesel source in the United States while many European countries are concerned with rapeseed oil, and countries with tropical climate prefer to utilize coconut oil or palm oil.

Palm oil is widely grown in South East Asia and 90% of the palm oil produced is used for food and the remaining 10% for non-food consumption, such as production of oleo-chemicals (Leng *et al.*, 1999). An alternative use could be its conversion to liquid fuels and chemicals. Conversion of palm oil to biodiesel using methanol has been reported (Yarmo *et al.*, 1992). There are great differences between palm oil and palm kernel oil in physical and chemical characteristics. Palm oil contains mainly palmitic (16:0) and oleic (18:1) acids, the two common fatty acids and about 50% saturated acids, while palm kernel oil contains mainly lauric acid (12:0) and more than 89% saturated acids (Demirbas, 2003c).

Rapeseed had been grown in Canada since 1936. Hundreds of years ago, Asians and Europeans used rapeseed oil in lamps. Cottonseed oil is used almost entirely as a food material. Sesame, olive, and peanut oils can be used to add flavor to a dish. Walnut oil is high quality edible oil refined by purely physical means from quality walnuts. Poppy seeds are tiny seeds contained within the bulb

of the poppy flower, also known as the opium plant (*Papaver somniferum*). Poppy seed oil is high in linoleic acid (typically 60–65%) and oleic acid (typically 18–20%) (Bajpai *et al.*, 1999).

Table 4.17 shows the comparisons of some fuel properties of vegetable oils with No. 2 diesel fuel. The heat contents of vegetable oils are approximately 88% of that of No. 2 diesel. There is little difference between the gross heat content of any of the vegetable oils (Demirbas, 1998). The density values of vegetable oils are between 912 and 921 kg/m³ while that of No. 2 diesel fuel is 815 kg/m³. The kinematic viscosity values of vegetable oils vary between 39.2 and 65.4 mm²/s at 300 K. The vegetable oils were all extremely viscous, with viscosities 8–15 times greater than No. 2 diesel fuel (Table 4.17).

12 (cottonseed, poppyseed, rapeseed, safflower seed, sunflower seed, soybean, corn marrow, sesame seed, linseed, castor, wheat grain, and bay laurel leaf) and 5 kernels (peanut, hazelnut, walnut, almond, and olive) samples used in this study were supplied from different Turkish agricultural sources. Physical analyses of the samples were carried out according to standard test methods: ASTM D445, ASTM D613, and ASTM D524 for kinematic viscosity (KV), cetane number (CN), and carbon residue (CR), respectively. However, as too low amounts of wheat grain, bay laurel leaf, and corn marrow oils were available for determination of cetane numbers using the standard method a calculated cetane number was established as according to Goering *et al.* (1982). Chemical analyses of the samples were carried out according to the standard test methods: ASTM D 2015-85, ASTM D5453-93, ASTM D482-91, AOCS CD1-25, and AOCS CD3 for higher heating value (HHV), sulfur content (SC), ash content (AC), iodine value (IV), and saponification value (SV), respectively. The other standard test methods for fuel properties are presented in Table 4.18. Fatty acid compositions of oil samples were determined by GC analysis. The oil samples were saponified for 3.5 h and 338 K with 0.5 N methanolic KOH to liberate the fatty acids present as their esters. After acidification of the saponified solutions with 1.5 N HCl acid, the acids were weighed and methylated with diazomethane according to the method of Schelenk and Gellerman (1960). The methyl esters of the fatty acids were analyzed by GC (Hewlett–Packard 5790) on a 12 m long and 0.2 mm inside diameter capillary

Table 4.17 Comparisons of some fuel properties of vegetable oils with No. 2 diesel fuel

Fuel type	Heating value (MJ/kg)	Density (kg/m ³)	Viscosity at 300 K (mm ² /s)	Cetane number ^a
No. 2 diesel fuel	43.4	815	4.3	47.0
Sunflower oil	39.5	918	58.5	37.1
Cottonseed oil	39.6	912	50.1	48.1
Soybean oil	39.6	914	65.4	38.0
Corn oil	37.8	915	46.3	37.6
Opium poppy oil	38.9	921	56.1	–
Rapeseed oil	37.6	914	39.2	37.6

^aCetane number (CN) is a measure of ignition quality of diesel fuel.

column coated with Carbowax PEG 20. The detector was a FID. Helium was used as a carrier gas. The flame ionization detector temperature was 500 K. The oven temperature was kept at 450 K for 25 min. After that, the oven was heated with heat ratio 5 K/min to 495 K. The spectra of methyl esters were recorded with a VG 70-250-SE mass spectrometer with double focusing. Ionization was carried out at 70 eV. The mass spectrometer was fitted to the gas chromatograph by means of a capillary glass jet separator.

Table 4.19 lists the physical and chemical properties of the oil samples. Viscosity values (KV) of the oil samples range from 23.2–42.4 mm²/s at 311 K. Vegeta-

Table 4.18 Determination of physical and chemical properties using standard test methods

Property	Symbol	Standard method	Unit
Density	d	ASTM D4052-91	g/ml
Iodine value	IV	AOCS CD1-25 1993	centigram I/g oil
Saponification value	SV	AOCS CD3 1993	mg KOH/g oil
Higher heating value	HHV	ASTM D2015-85	MJ/kg
Cloud point	CP	ASTM D2500-91	K
Pour point	PP	ASTM D97-93	K
Flash point	FP	ASTM D93-94	K
Cetane number	CN	ASTM D613	—
Kinematic viscosity	KV	ASTM D445	mm ² /s at 311 K
Sulfur content	SC	ASTM D5453-93	wt%
Carbon residue	CR	ASTM D 524	wt%
Ash content	AC	ASTM D482-91	wt%

Table 4.19 Physical and chemical properties of oil samples

Vegetable oil	KV	CR	CN	HHV	AC	SC	IV	SV
Cottonseed	33.7	0.25	33.7	39.4	0.02	0.01	113.20	207.71
Poppyseed	42.4	0.25	36.7	39.6	0.02	0.01	116.83	196.82
Rapeseed	37.3	0.31	37.5	39.7	0.006	0.01	108.05	197.07
Safflower seed	31.6	0.26	42.0	39.5	0.007	0.01	139.83	190.23
Sunflower seed	34.4	0.28	36.7	39.6	0.01	0.01	132.32	191.70
Sesame seed	36.0	0.25	40.4	39.4	0.002	0.01	91.76	210.34
Linseed	28.0	0.24	27.6	39.3	0.01	0.01	156.74	188.71
Wheat grain	32.6	0.23	35.2	39.3	0.02	0.02	120.96	205.68
Corn marrow	35.1	0.22	37.5	39.6	0.01	0.01	119.41	194.14
Castor	29.7	0.21	42.3	37.4	0.01	0.01	88.72	202.71
Soybean	33.1	0.24	38.1	39.6	0.006	0.01	69.82	220.78
Bay laurel leaf	23.2	0.20	33.6	39.3	0.03	0.02	105.15	220.62
Peanut kernel	40.0	0.22	34.6	39.5	0.02	0.01	119.55	199.80
Hazelnut kernel	24.0	0.21	52.9	39.8	0.01	0.02	98.62	197.63
Walnut kernel	36.8	0.24	33.6	39.6	0.02	0.02	135.24	190.82
Almond kernel	34.2	0.22	34.5	39.8	0.01	0.01	102.35	197.56
Olive kernel	29.4	0.23	49.3	39.7	0.008	0.02	100.16	196.83

ble oils are all extremely viscous, with viscosities ranging from 10–20 times that of the ASTM upper limit given for diesel fuels ($2.7 \text{ mm}^2/\text{s}$).

Higher heating values (HHVs) of the oil samples range from 39.3 to 39.8 MJ/kg. Castor oil has exceptional HHV (37.4 MJ/kg). The oxygen content of castor oil is higher than those of vegetable oils due to ricinoleic acid in its structure. Ricinoleic is the only 18:1 fatty acid that contains a hydroxyl group. Because castor oil contains a hydroxyl group, its HHV is lower than that of other oils.

Cetane numbers (CNs) of the oil samples range from 27.6–52.9. Iodine values (IVs) and saponification values (SVs) of the oil samples range from 69.82–156.74 and from 188.71–220.78, respectively.

The saponification value (SV) of an oil decreases with increase of its molecular weight. The percentages of C and H in an oil decrease with increase in molecular weight. The increase in SV results in a decrease in the heat content of an oil. The increase in iodine value (IV) (*i.e.*, carbon–carbon double bond, $-\text{C}=\text{C}-$, content of oil) results in a decrease in the heat content of an oil. The heat contents of the oil depend on the saponification and iodine values. Therefore, for calculation of the HHVs (MJ/kg) of oil samples, Eq. 4.16 was suggested (Demirbas, 1998).

$$\text{HHV} = 49.43 - 0.041 (\text{SV}) - 0.015 (\text{IV}) \quad (4.16)$$

Thus the heating values of the vegetable oils can be calculated by using their SVs and IVs obtained from simple chemical analyses without using a calorimeter.

The carbon residues (CRs), sulfur contents (SCs) and ash contents (ACs) of the oil samples range from 0.20–0.31 wt.%, from 0.01–0.02 wt.%, from 0.002–0.02 wt.%, respectively (Table 4.19).

The increase in heat content results from a high increase in the number of carbons and hydrogens, as well as an increase in the ratio of these elements relative to oxygen. A decrease in heat content is the result of fewer hydrogen atoms (*i.e.*, greater unsaturation) in the fuel molecule. Determination of data obtained for a great many compounds has shown that the HHV of an aliphatic hydrocarbon agrees rather closely with that calculated by assuming a certain characteristic contribution from each structural unit (Morrison and Boyd, 1983). For open-chain alkanes, each methylene group, $-\text{CH}_2-$, contributes very close to 46,956 kJ/kg.

4.5.3.1 Direct Use of Vegetable Oils in Diesel Engines

The use of vegetable oils as alternative renewable fuel competing with petroleum was proposed in the beginning of 1980s. The advantages of vegetable oils as diesel fuel are (Demirbas, 2003b): (a) liquid nature-portability, (b) ready availability, (c) renewability, (d) higher heat content (about 88% of No. 2 diesel fuel), (e) lower sulfur content, (f) lower aromatic content, and (g) biodegradability,

Full combustion of a fuel requires in existence the amount of stoichiometric oxygen. However, the amount of stoichiometric oxygen generally is not enough for full combustion so as not to oxygenate the fuel. The structural oxygen content of fuel increases combustion efficiency of the fuel due to increased mixing of

oxygen with the fuel during combustion. For these reasons, the combustion efficiency and cetane number of vegetable oil is higher than that of diesel fuel and the combustion efficiency methanol and ethanol is higher than that of gasoline.

The main disadvantages of vegetable oils as diesel fuel are (Pryde, 1983): (a) higher viscosity, (b) lower volatility, and (c) the reactivity of unsaturated hydrocarbon chains.

Problems appear only after the engine has been operating on vegetable oils for longer periods of time, especially with direct-injection engines. The problems include: (a) coking and trumpet formation on the injectors to such an extent that fuel atomization does not occur properly or is even prevented as a result of plugged orifices, (b) carbon deposits, (c) oil ring sticking and (d) thickening and gelling of the lubricating oil as a result of contamination by the vegetable oils (Ma and Hanna, 1999).

Among the renewable resources for the production of alternative fuels, triglycerides have attracted much attention as alternative diesel engine fuels (Shay, 1993). However, the direct use of vegetable oils and/or oil blends is generally considered to be unsatisfactory and impractical for both direct injection and indirect type diesel engines because of their high viscosity and low volatility, injector coking and trumpet formation on the injectors, more carbon deposits, oil ring sticking, and thickening and gelling of the engine lubricant oil, acid composition (the reactivity of unsaturated hydrocarbon chains), and free fatty acid content (Ma and Hanna, 1999; Darnoko and Cheryan, 2000; Srivastava and Prasad, 2000; Komers *et al.* 2001). Consequently, different ways have been considered to reduce the viscosity of vegetable oils such as dilution, microemulsification, pyrolysis, catalytic cracking, and transesterification. Methods based on pyrolysis (Dandik and Aksoy, 1998; Bhatia *et al.*, 1998; Lima *et al.*, 2004) and microemulsification (Billaud *et al.*, 1995) have been studied but are not entirely satisfactory.

Vegetable oils can be used as fuels for diesel engines, but their viscosities are much higher than usual diesel fuel and require modifications of the engines (Kerschbaum and Rinke, 2004). Vegetable oils can possibly only replace a very small fraction of transport fuel. Different ways have been considered to reduce the high viscosity of vegetable oils:

1. Dilution of 25 parts of vegetable oil with 75 parts of diesel fuel.
2. Microemulsions with short chain alcohols such as ethanol or methanol.
3. Transesterification with ethanol or methanol, which produces biodiesel.
4. Pyrolysis and catalytic cracking, which produces alkanes, cycloalkanes, alkenes, and alkylbenzenes.

Dilution of oils with solvents and microemulsions of vegetable oils lowers the viscosity, some engine performance problems, such as injector coking and more carbon deposits, *etc.* To dilute vegetable oils the addition of 4% ethanol increases the brake thermal efficiency, brake torque, and brake power, while decreasing brake specific fuel consumption. Since the boiling point of ethanol is less than those of vegetable oils the development of the combustion process may be assisted through unburned blend spray (Bilgin *et al.*, 2002).

The viscosity of oil can be lowered by blending with pure ethanol. 25 parts sunflower oil and 75 parts diesel have been blended as diesel fuel (Ziejewski *et al.*, 1986). The viscosity was 4.88 cSt at 313 K, while the maximum specified ASTM value is 4.0 cSt at 313 K. This mixture was not suitable for long-term use in a direct injection engine. Another study was conducted by using the dilution technique on the same frying oil (Karaosmonoglu, 1999).

The addition of 4% ethanol to No. 2 diesel fuel increases brake thermal efficiency, brake torque, and brake power, while decreasing the brake specific fuel consumption. Since the boiling point of ethanol is less than that of D2 fuel, it may assist the development of the combustion process through an unburned blend spray (Bilgin *et al.*, 2002).

To reduce the high viscosity of vegetable oils, microemulsions with immiscible liquids such as methanol, ethanol, and ionic or non-ionic amphiphiles have been studied (Billaud *et al.*, 1995). Short engine performances of both ionic and non-ionic microemulsions of ethanol in soybean oil were nearly as good as that of No. 2 diesel fuel (Goering *et al.*, 1982). To solve the problem of the high viscosity of vegetable oils, microemulsions with solvents such as methanol, ethanol, and 1-butanol have been studied. All microemulsions with butanol, hexanol, and octanol met the maximum viscosity requirement for No. 2 diesel fuel. The 2-octanol was found to be an effective amphiphile in the micellar solubilization of methanol in triolein and soybean oil (Schwab *et al.*, 1987; Ma and Hanna, 1999).

Ziejewski *et al.* (1986) prepared an emulsion of 53% (vol) alkali-refined and winterized sunflower oil, 13.3% (vol) 190-proof ethanol and 33.4% (vol) 1-butanol. This non-ionic emulsion had a viscosity of 6.31 cSt at 313 K, a cetane number of 25, and an ash content of less than 0.01%. Lower viscosities and better spray patterns (more even) were observed with an increase of 1-butanol. In a 200 h laboratory screening endurance test, no significant deteriorations in performance were observed, but irregular injector needle sticking, heavy carbon deposits, incomplete combustion, and an increase of lubricating oil viscosity were reported (Ma and Hanna, 1999).

A microemulsion prepared by blending soybean oil, methanol, 2-octanol, and cetane improver in the ratio of 52.7:13.3:33.3:1.0 also passed the 200 h EMA test (Goering, 1984). Schwab *et al.* (1987) used the ternary phase equilibrium diagram and the plot of viscosity *versus* solvent fraction to determine the emulsified fuel formulations. All microemulsions with butanol, hexanol, and octanol met the maximum viscosity requirement for No. 2 diesel. The 2-octanol was an effective amphiphile in the micellar solubilization of methanol in triolein and soybean oil. Methanol was often used due to its economic advantage over ethanol.

Among all these alternatives, transesterification seems to be the best choice, as the physical characteristics of fatty acid esters (biodiesel) are very close to those of diesel fuel, and the process is relatively simple. In the esterification of an acid, an alcohol acts as a nucleophilic reagent; in hydrolysis of an ester, an alcohol is displaced by a nucleophilic reagent. This alcoholysis (cleavage by an alcohol) of an ester is called transesterification (Gunstone and Hamilton, 2001).

Transesterified vegetable oils have proven to be a viable alternative diesel engine fuel with characteristics similar to those of diesel fuel. The transesterification reaction proceeds with a catalyst or any unused catalyst by using primary or secondary monohydric aliphatic alcohols having 1–8 carbon atoms as follows. Transesterification is catalyzed by a base (usually alkoxide ion) or acid (H_2SO_4 or dry HCl). The transesterification is an equilibrium reaction. To shift the equilibrium to the right, it is necessary to use a large excess of the alcohol or else to remove one of the products from the reaction mixture. Furthermore, the methyl or ethyl esters of fatty acids can be burned directly in unmodified diesel engines, with very low deposit formation. Although short-term tests using neat vegetable oil showed promising results, longer tests led to injector coking, more engine deposits, ring sticking, and thickening of the engine lubricant. These experiences led to the use of modified vegetable oil as a fuel.

Technical properties of biodiesel, such as the physical and chemical characteristics of methyl esters related are close to, such as physical and chemical characteristics of methyl esters related to its performance in compression ignition engines are close to petroleum diesel fuel (Saucedo, 2001). Compared with transesterification, the pyrolysis process has more advantages. The liquid fuel produced from pyrolysis has similar chemical components to conventional petroleum diesel fuel (Zhenyi *et al.*, 2004).

4.5.4 New Biorenewable Fuels from Vegetable Oils

World annual petroleum consumption and vegetable oil production is about 4.018 and 0.107 billion tons, respectively. Vegetable oils from bio renewable oil seeds can be used when mixed with diesel fuels. Vegetable oils can be used as fuels for diesel engines, but their viscosities are much higher than usual diesel fuel and require modifications of the engines. Different ways have been considered to reduce the viscosity of vegetable oils such as dilution, microemulsification, pyrolysis, catalytic cracking, and transesterification. Compared with transesterification, the pyrolysis process has more advantages. The liquid fuel produced from pyrolysis has similar chemical components to conventional petroleum diesel fuel. Vegetable oils can be converted to a maximum of liquid and gaseous hydrocarbons by pyrolysis, decarboxylation, deoxygenation, and catalytic cracking processes.

Pyrolysis utilizes biomass to produce a product that is used both as an energy source and a feedstock for chemical production (Demirbas, 2000). A current comprehensive review focuses on the recent developments in the biomass pyrolysis and reports the characteristics of the resulting bio-oils, which are the main products of pyrolysis (Mohan *et al.*, 2006).

Triglycerides are esters of glycerin with different fatty acids. The proportions of the various acids vary from oil to oil; each oil has its own characteristic composition. Triglyceride vegetable oils and fats include not only edible, but also inedible vegetable oils and fats such as linseed oil, castor oil, and tung oil.

Vegetable oils have the potential to substitute a fraction of petroleum distillates and petroleum-based petrochemicals in the near future. Possible acceptable converting processes of vegetable oils into reusable products are transesterification, solvent extraction, cracking, and pyrolysis (Bhatia *et al.*, 1998). Pyrolysis has received a significant amount of interest as this gives products of better quality compared to any other thermochemical process. The liquid fuel produced from vegetable oil pyrolysis has similar chemical components to conventional petroleum diesel fuel. Pyrolysis of triglycerides has been investigated for more than 100 years, especially in areas of the world that lack deposits of petroleum (Zhenyi *et al.*, 2004).

Vegetable oils are biorenewable and potentially inexhaustible sources of energy with energetic contents close to diesel fuel. There are more than 350 identified oil-bearing crops, among which only sunflower, safflower, soybean, cottonseed, rapeseed, and peanut oils are considered as potential alternative fuels for diesel engines (Goering *et al.*, 1982; Pryor *et al.*, 1982). The major problem associated with the use of pure vegetable oils as fuels, for diesel engines are caused by high fuel viscosity in compression ignition.

Because of the possibility of production in wide variety of products by the high temperature pyrolysis reactions, many investigators have studied the pyrolysis of plant oils to obtain products suitable for fuel under different reaction conditions with and without catalysts (Dandik and Aksoy, 1998; Bhatia *et al.*, 1999; Lima *et al.*, 2004).

4.5.4.1 New Transportation Fuels from Vegetable Oils *via* Pyrolysis

Limitations to vegetable oil use are costs and potential production. Production of vegetable oil is limited by the land area available. Vegetable oil fuels are not petroleum-competitive fuels because they are more expensive than petroleum fuels. However, with recent increases in petroleum prices and uncertainties concerning petroleum availability, there is renewed interest in using vegetable oils in diesel engines.

Biodiesel is a fuel consisting of long-chain fatty acid alkyl esters made from renewable vegetable oils, recycled cooking greases, or animal fats. Vegetable oils are generally converted to their methyl esters by transesterification reaction in the presence catalyst. Methyl esters of vegetable oils (biodiesels) have several outstanding advantages among other new-renewable and clean engine fuel alternatives. Compared to No. 2 diesel fuel, all vegetable oils are much more viscous, while methyl esters of vegetable oils are the slightly more viscous. The methyl esters are more volatile than those of the vegetable oils.

The soaps obtained from the vegetable oils can be pyrolyzed into hydrocarbon-rich products (Demirbas, 2002). Pyrolysis of Na-soaps may be obtained from vegetable oil as follows:

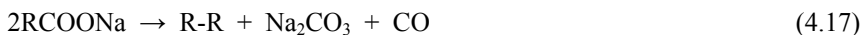


Table 4.20 Yields of pyrolysis products from used sunflower oil sodium soaps at different temperatures (% by weight)

400 K	450 K	500 K	520 K	550 K	570 K	590 K	610 K
2.8	8.4	29.0	45.4	62.4	84.6	92.7	97.5

Source: Demirbas, 2002

The soaps obtained from the vegetable oils can be pyrolyzed into hydrocarbon-rich products according to Eq. 4.17 with higher yields at lower temperatures (Demirbas, 2002). Table 4.20 shows the yields of pyrolysis products from used sunflower oil sodium soaps at different temperatures. These findings are in general agreement with results given in the literature (Barsic and Humke, 1981).

Pyrolysis of used sunflower oil was carried out in a reactor equipped with a fractionating packed column at 673 and 693 K in the presence of sodium carbonate (1, 5, 10, and 20% based on oil weight) as a catalyst. The conversion of oil was high (42–83 wt%) and the product distribution depended strongly on the reaction temperature, residence times, and catalyst content. The pyrolysis products consisted of gas and liquid hydrocarbons, carboxylic acids, CO, CO₂, H₂ and water (Dandik and Aksoy, 1998).

The three vegetable oils (soybean, palm, and castor oils) were pyrolyzed to obtain light fuel products at 503–673 K (Lima *et al.*, 2004). These results show that the soybean, palm, and castor oils present a similar behavior considering the pyrolysis temperature range. On the other hand, palm oil reacts in a lower temperature range with a higher yield in the heavy fraction (Lima *et al.*, 2004). Short pyrolysis time (less than 10 s) leads to a high amount of alkanes, alkenes and aldehydes instead of carboxylic acids. On the other hand, higher temperature and long pyrolysis time did not favor an extensive pyrolysis of this material. In this case, desorption like process becomes more likely than the pyrolytic process (Lima *et al.*, 2004; Fortes and Baugh, 1999). The parameters of the pyrolysis systematically affected the pyrolytic process.

An increase of Na₂CO₃ content and the temperature increased the formation of liquid hydrocarbon and gas products and decreased the formation of aqueous phase, acid phase and coke–residual oil. The highest C₅–C₁₁ yield (36.4%) was obtained by using 10% Na₂CO₃ and a packed column of 180 mm at 693 K. The use of packed column increased the residence times of the primer pyrolysis products in the reactor, which caused catalytic and thermal degradation reactions (Dandik and Aksoy, 1998).

The properties of pyrolysis oil from rapeseed are given in Table 4.21. The higher heating value of pyrolysis oil from vegetable oils is quite high. The higher heating value of pyrolysis oil from rapeseed (38.4 MJ/kg) is slightly lower than that of gasoline (47 MJ/kg), diesel fuel (43 MJ/kg) or petroleum (42 MJ/kg), but higher than coal (32–37 MJ/kg) (Sensoz *et al.*, 2000).

Table 4.22 shows the yields of ZnCl₂ catalytic pyrolysis from sunflower oil at different temperatures (Demirbas, 2003b). Yield of conversion to products of

ZnCl₂ catalytic pyrolysis from the sunflower oil increased with the increase in reaction temperature. The yield of conversion to the products from the sunflower oil reached the maximum 78.3% at 660 K. The decrease in yield of conversion could probably be due to higher coke and gas formation at the pyrolysis temperatures higher than 660 K. As more coke might be deposited on the catalyst's surface the effect of pyrolysis reduced. The gasoline content reached a maximum (35.8% of the conversion products) at 660 K. The aromatic and gas oil contents of conversion products showed a similar trend (Demirbas, 2003b).

Thermal degradation of aliphatic long chain compounds is known as cracking. Higher molecules generally convert into smaller molecules by the cracking process. Large alkane molecules are converted into smaller alkanes and some hydrogen in the cracking process. The smaller hydrocarbons can be obtained by hydrocracking process. Hydrocracking is carried out in the presence of a catalyst and hydrogen, at high pressure and at much lower temperatures (525–725 K).

Table 4.21 Properties of pyrolysis oil from rapeseed

Properties	Methods	Pyrolysis oil
Density, 303 K (kg/m ³)	ASTM D 1298	918
Water content (w/w%)	ASTM D 1744	None
Viscosity, 323 K (cSt)	ASTM D 88	43
Flash point (K)	ASTM D 93	359
Conradson residue (w/w%)	ASTM D 189	0.05
Heating value (MJ/kg)	ASTM D 3286	38.4
<i>Elemental analysis (w/w%)</i>		
Carbon	ASTM D 482	74.04
Hydrogen	ASTM D 3177	10.29
Oxygen (by diff.)		11.70
Nitrogen		3.97
H/C Molar ratio	Calculation	1.67
O/C Molar ratio	Calculation	0.12
Empirical formula	Calculation	CH _{1.67} O _{0.12} N _{0.046}

Table 4.22 Yields of ZnCl₂ catalytic pyrolysis from sunflower oil (SFO) at different temperatures

Temperature (K)	610	630	650	660	670	690
Conversion, wt% of SFO	35.6	60.7	71.5	78.3	74.9	68.4
Gaseous product, wt%	3.4	5.1	6.4	7.0	8.9	10.6
Aromatic content, wt%	8.5	9.3	9.0	9.6	8.2	8.8
Gasoline content, wt%	28.6	30.4	29.4	35.8	32.7	29.3
Gas oil content, wt%	6.6	7.3	8.4	10.7	8.6	7.9
Coke residue, wt%	0.2	0.3	0.4	0.5	2.4	6.8
Water formation, wt%	3.4	3.7	4.1	4.5	4.1	3.8
Unidentified, wt%	49.3	43.9	42.3	31.9	35.1	32.8

Source: Demirbas, 2003b

Higher boiling petroleum fractions (typically, gas oil) are obtained from silica-alumina catalytic cracking at 725–825 K and under lower pressure. The catalytic cracking not only increases the yield of gasoline by breaking large molecules into smaller ones, but also improves the quality of the gasoline: this process involves carbocations (a group of atoms that contains a carbon atom bearing only six electrons)

Palm oil stearin and copra oil was subjected to conversion over different catalysts, like silica-alumina and zeolite (Pioch *et al.*, 1993). It was found that the conversion of palm and copra oil was 84 wt% and 74 wt%, respectively. The silica-alumina catalyst was highly selective for obtaining aliphatic hydrocarbons, mainly in the kerosene boiling point range (Katikaneni, 1995). The organic liquid products obtained with the silica-alumina catalyst contained between 4–31 wt% aliphatic hydrocarbons and 14–58 wt% aromatic hydrocarbons. The conversion was high and ranged between 81 wt% and 99 wt%. Silica-alumina catalysts are suitable for converting vegetable oils to aliphatic hydrocarbons. The zinc chloride catalyst, as a Lewis acid, contributes to hydrogen transfer reactions and formation of hydrocarbons in the liquid phase. Palm oil has been converted to hydrocarbons using a shape selective zeolite catalyst (Leng *et al.*, 1999). Palm oil can be converted to aromatics and hydrocarbons in the gasoline, diesel and kerosene range, light gases, and coke and water with the yield of 70 wt%. The maximum yield of gasoline range hydrocarbons was 40 wt% of the total product.

Palm oil has been cracked at atmospheric pressure, at a reaction temperature of 723 K to produce biofuel in a fixed-bed microreactor. The reaction was carried out over microporous HZSM-5 zeolite, mesoporous MCM-41, and composite micromesoporous zeolite as catalysts. The products obtained were gas, organic liquid, water, and coke. The organic liquid product was composed of hydrocarbons corresponding to gasoline, kerosene, and diesel boiling point range. The maximum conversion of palm oil, 99 wt%, and gasoline yield of 48 wt% was obtained with composite micromesoporous zeolite. Table 4.23 presents the conversion of palm oil over HZSM-5 with different Si/Al ratios of catalysts by catalytic cracking (Sang *et al.*, 2003). The gasoline yield increased with the increase in the Si/Al ratio due to the decrease in the secondary cracking reactions and the drop in the yield of gaseous products. The vegetable oils were converted to liquid products

Table 4.23 Catalytic cracking of palm oil over HZSM-5 with different Si/Al ratios

Catalyst ID	HZSM-5(50)	HZSM-5(240)	HZSM-5(400)
Conversion (wt%)	96.9	96.0	94.0
Gas yield (wt%)	17.5	14.0	8.2
Water yield (wt%)	6.8	4.6	6.1
OLP (wt%)			
Total organic liquid yield	70.9	76.0	78.0
Gasoline (wt%)	44.6	45.9	49.3
Kerosene (wt%)	19.6	24.6	26.1
Diesel (wt%)	6.7	5.5	2.6
Coke (wt%)	1.7	1.4	1.7

containing gasoline boiling range hydrocarbons. The results show that the product compositions are affected by catalyst content and temperature.

4.5.4.2 Pyrolysis Mechanisms of Vegetable Oils

Soybean, rapeseed, sunflower, and palm oils have been the most studied for the preparation of bio-oil. The viscosity of the distillate was $10.2 \text{ mm}^2/\text{s}$ at 311 K, which is higher than the ASTM specification for No. 2 diesel fuel ($1.9\text{--}4.1 \text{ mm}^2/\text{s}$) but considerably below that of soybean oil ($32.6 \text{ mm}^2/\text{s}$). Used cottonseed oil from the cooking process was decomposed with Na_2CO_3 as catalyst at 725 K to give a pyrolyzate containing mainly C_{8-20} alkanes (69.6%) besides alkenes and aromatics. The pyrolyzate had lower viscosity, pour point, and flash point than No. 2 diesel fuel and equivalent heating values (Bala, 2005).

A mechanism for catalytic decarboxylation of vegetable oils is proposed in Fig. 4.7. Vegetable oils contain mainly palmitic, stearic, oleic, and linoleic acids. These fatty acids underwent various reactions, resulting in the formation of different types of hydrocarbons.

The variety of reaction paths and intermediates makes it difficult to describe the reaction mechanism. Besides, the multiplicity of possible reactions of mixed triglycerides make the pyrolysis reaction more complicated (Zhenyi *et al.*, 2004). Generally, thermal decomposition of triglycerides proceed through either a free-radical or carbonium ion mechanism (Srivastava and Prasad, 2000).

Vegetable oil is converted to lower molecular products by two simultaneous reactions: cracking and condensation. In a first step of pyrolysis the triglycerides are converted into carboxylic acids, which are further decomposed by decarboxylation (leading to alkanes and carbon dioxide) or decarbonylations (forming alkenes, water and carbon monoxide) (Gusmao, *et al.*, 1989).

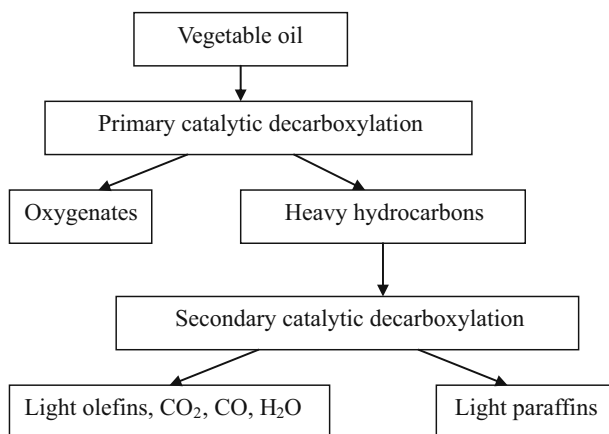


Fig. 4.7 Reaction pathway of catalytic decarboxylation of vegetable oils

The distributions of pyrolysis products depend on the dynamics and kinetics control of different reactions. Maximum of gasoline fraction can be obtained under appropriate reaction conditions. Thermodynamic calculation shows that the initial decomposition of vegetable oils occurs with the breaking of the C–O bond at lower temperature, and fatty acids are the main product. The pyrolysis temperature should be higher than 675 K; at this temperature, the maximum of diesel yield with high content of oxygen can be obtained (Zhenyi *et al.*, 2004). The effect of temperature, the use of catalysts, and the characterization of the products have been investigated (Srivastava and Prasad, 2000). In pyrolysis, the high molecular materials are heated to high temperatures, so their macromolecular structures are broken down into smaller molecules, and a wide range of hydrocarbons are formed. These pyrolytic products can be divided into a gas fraction, a liquid fraction consisting of paraffins, olefins and naphthenes, and solid residue. The cracking process yields a highly unstable low-grade fuel oil, which can be acid-corrosive, tarry, and discolored along with a characteristically foul odor (Demirbas, 2004b).

It has been proposed that thermal and catalytic cracking of triglyceride molecules occurs at the external surface of the catalysts to produce small molecular size components, comprising of mainly heavy liquid hydrocarbons and oxygenates (Demirbas, 2004). In general, it is assumed that the reactions predominantly occur within the internal pore structure of zeolite catalyst.

The catalyst acidity and pore size affect the formation of aromatic and aliphatic hydrocarbons. Hydrogen transfer reactions, which are essential for hydrocarbon formation, are known to increase with catalyst acidity. The high acid density of ZnCl_2 catalyst contributes greatly to high amounts of hydrocarbons in the liquid product.

Pyrolysis is the conversion of one substance into another by means of heat or by heat with the aid of a catalyst (Sonntag, 1979). It involves heating in the absence of air or oxygen and cleavage of chemical bonds to yield small molecules. The pyrolyzed material can be vegetable oils, animal fats, natural fatty acids, and methyl esters of fatty acids.

Catalytic cracking of vegetable oils to produce biofuels has been studied (Pioch *et al.*, 1993). Copra oil and palm oil stearin were cracked over a standard petroleum catalyst $\text{SiO}_2/\text{Al}_2\text{O}_3$ at 723 K to produce gases, liquids and solids with lower molecular weights. The condensed organic phase was fractionated to produce biogasoline and biodiesel fuels.

Pyrolysis liquid products of vegetable oils can be used as alternative engine fuel. Vegetable oils may be converted to liquid product containing gasoline boiling range hydrocarbons. The product compositions are affected by catalyst content and temperature. In pyrolysis, the high molecular materials are heated to high temperatures, so their macromolecular structures are broken down into smaller molecules and a wide range of hydrocarbons are formed.

A single-step direct process for the production of gasoline-like fuel catalytic pyrolysis of vegetable oil is a promising alternative route for environmentally friendly liquid fuels. Vegetable oil has been cracked to obtain liquid fuels at atmospheric pressure, with a reaction temperature of 700–750 K in the presence zeolite as catalysts. The products obtained were gas, organic liquid product, water,

and coke. The organic liquid product was composed of hydrocarbons corresponding to gasoline, kerosene, and diesel boiling point range.

4.5.4.3 Gasoline-rich Liquid from Sunflower Oil by Alumina Catalytic Pyrolysis

Recycling and re-refining are the applicable processes for upgrading of vegetable oils by converting them into reusable products such as gasoline and diesel fuel. Possible acceptable processes are transesterification, cracking, and pyrolysis.

The samples of sunflower seed oil were used in the experiments. The sunflower oils were obtained from commercial sources and used without further purification. Aluminum oxide (Al_2O_3 , also known as alumina) was obtained from bauxite by the caustic leach method. The catalyst was treated with 10% sodium hydroxide solution before using in the pyrolysis. 2.5 g of NaOH and 25 g alumina (Al_2O_3) were added to 250 ml of deionized water with stirring in a water bath for 45 minutes. 0.5 g of AlCl_3 was slowly added to the mixture and stirred vigorously for 30 minutes. The solid material was thoroughly washed, filtered, dried at room temperature overnight, and then calcined at 850 K for 6 h. The pyrolysis experiments were performed on a laboratory scale apparatus. The main element of this device was a vertical cylindrical reactor of stainless-steel, 127.0 mm height, 17.0 mm inner diameter, and 25.0 mm outer diameter inserted vertically into an electrically heated furnace and provided with an electrical heating system power source.

Heat to the vertical cylindrical reactor was supplied from external heater and the power was adjusted to give an appropriate heat up time. The simple thermocouple (NiCr–Constantan) or a 360° degree thermometer with mercury was placed directly in the pyrolysis medium. For each run, the heater was started at 298 K and terminated when the desired temperature was reached. The sunflower seed oil samples were treated with 3% sodium hydroxide solutions in a separatory funnel and then washed with water before pyrolysis. The catalyst (1%, 3%, 4%, and 5% by weight of used sample) was used in the pyrolysis experiments. In addition, the sunflower seed oil samples were pyrolyzed in catalytic runs with 2% and 5% potassium hydroxide. The pyrolysis products were collected within three different groups as condensable liquid products, non-condensable gaseous products, and solid residue. The liquid product was collected in two glass traps with cooled ice–salt mixture and ice, respectively. The gas products were trapped over a saturated solution of NaCl in a gas holder.

Figure 4.8 shows the plots for yield of liquid products from pyrolysis of the sunflower oil at different temperatures in the presence of KOH. The nominal pyrolysis time was 30 min. The yields of liquid products increase temperature and the amounts of KOH. The yield sharply increases between 580 K and 610 K and then it reaches a plateau value with 2% KOH run. Qualitative observations show that the pyrolytic liquid products from the runs with KOH are highly viscous as com-

pared with waste cooking sunflower oil. The repolymerization degree of the pyrolytic liquid products increases with increasing temperature.

Figure 4.9 shows the plots for the yields of liquid products from pyrolysis of the sunflower oil at different temperatures in the presence of an aluminum oxide

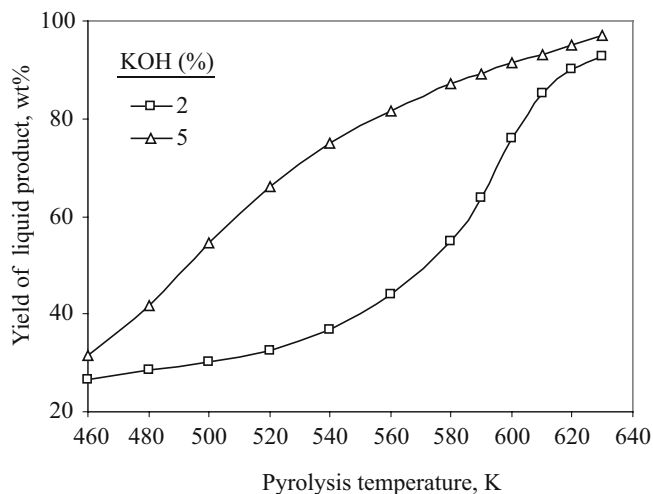


Fig. 4.8 Plots for yield of liquid products from pyrolysis of sunflower oil at different temperatures in the presence of KOH. Pyrolysis time: 30 min

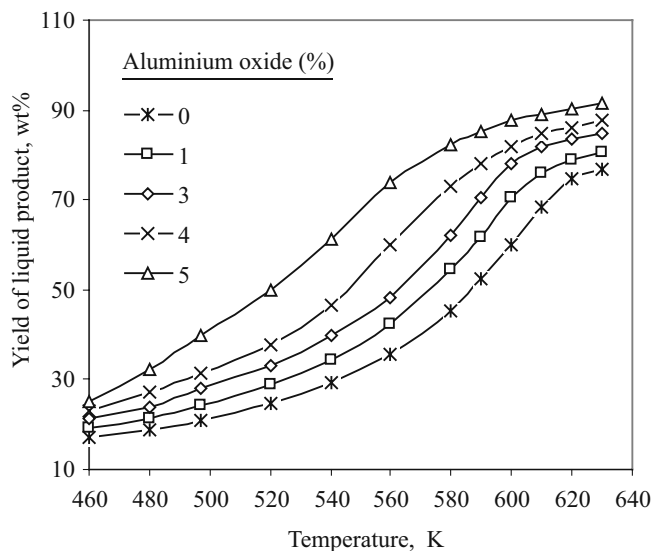


Fig. 4.9 Plots for yield of liquid products from pyrolysis of sunflower oil at different temperatures in the presence of aluminum oxide. Pyrolysis time: 30 min. Particle size: 80–120 mesh

catalyst, respectively. The catalyst was treated with 10% sodium hydroxide solution before being used in the pyrolysis. The particle size of the catalyst was between 80 mesh and 120 mesh. The yields of liquid products generally increase temperature and the percent of the catalyst.

From Fig. 4.9, the yield of liquid product from the sunflower oil sharply increases between 500 K and 680 K in 5% catalytic runs. The yields from non-catalytic runs were 22.1 and 76.8% at 500 and 630 K, respectively. The yields from 5% catalytic runs were 39.8 and 91.4% at 500 and 630 K, respectively. The yields of liquid products reach plateau values between 600 K and 630 K.

The liquid products from pyrolysis of used samples have gasoline-like fractions. Table 4.24 shows the average gasoline percentages of liquid products from pyrolysis of sunflower seed oil at different temperatures in the presence of sodium hydroxide treated aluminum oxide. As seen from Table 4.24, the properties of liquid products obtained from catalytic pyrolysis are similar to gasoline. The highest yields of gasoline were 53.8% for the gasoline from sunflower oil, which can be obtained from the pyrolysis with 5% catalytic runs.

Table 4.24 Average gasoline percentages of liquid products from pyrolysis of sunflower seed oil at different temperatures in the presence of aluminum oxide

Al ₂ O ₃ (%)	560 K	580 K	600 K	620 K	630 K
0	5.7	9.6	11.8	13.7	16.8
1	12.5	19.3	23.7	27.9	32.5
3	17.3	23.5	28.4	32.8	38.2
4	24.9	29.4	33.9	38.7	47.4
5	33.5	39.6	42.5	48.1	53.8

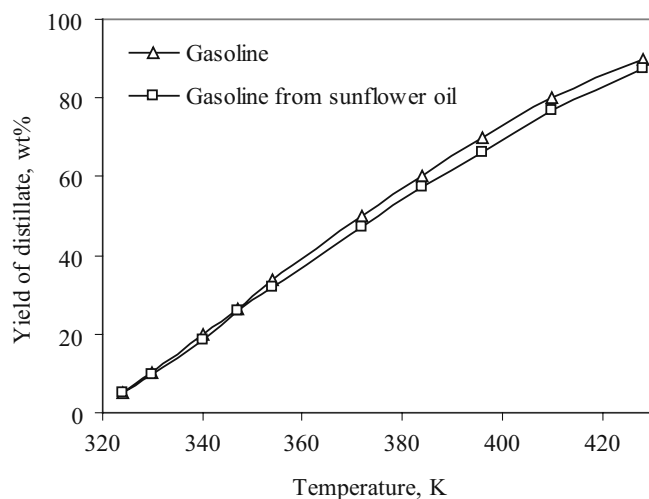


Fig. 4.10 Distillation curves of gasoline and sunflower oil gasoline

Figure 4.10 shows the curves of distillation of the petroleum-based gasoline and the gasoline from sunflower oil. The distillation curve of the gasoline from used lubricant oil by the catalytic pyrolysis is similar to that of gasoline. The petroleum-based gasoline is slightly more volatile than the sunflower oil gasoline.

4.5.5 Properties of Triglycerides

4.5.5.1 Emissions of Neat Vegetable Oil Fuel

While neat vegetable oils are competitive with conventional DF in some emission categories, problems were identified for other kinds of emissions. For example, it was shown that PAH emissions were lower for neat vegetable oils, especially very little amounts of alkylated PAHs, which are common in the emissions of conventional diesel fuel (Mills and Howard, 1983). Besides higher NO_x levels (Geyer *et al.*, 1984), aldehydes are reported to present problems with neat vegetable oils. Total aldehydes increased dramatically with vegetable oils (Geyer *et al.*, 1984).

4.5.5.2 Viscosity

Viscosity is a measure of the internal fluid friction or resistance of oil to flow, which tends to oppose any dynamic change in the fluid motion (Song, 2000). As the temperature of oil is increased its viscosity decreases and it is therefore able to flow more readily. It is also important for flow of oil through pipelines, injector nozzles and orifices (Radovanovic *et al.*, 2000). The lower the viscosity of the oil, the easier it is to pump and atomize and achieve finer droplets (Islam and Beg, 2004).

Viscosity is measured on several different scales, including Redwood No. 1 at 100F, Engler Degrees, Saybolt Seconds, *etc.* The Redwood viscosity value is the number of seconds required for 50 ml of an oil to flow out of a standard Redwood viscosimeter at a definite temperature. Viscosity is the most important property of biofuel since it affects the operation of fuel injection equipment, particularly at low temperatures when the increase in viscosity affects the fluidity of the fuel. Biodiesel has viscosity close to diesel fuels. High viscosity leads to poorer atomization of the fuel spray and less accurate operation of the fuel injectors.

The vegetable oils were all extremely viscous with viscosities of 10–20 times greater than No. 2 diesel fuel. Castor oil is in a class by itself with a viscosity more than 100 times that of No. 2 diesel fuel. The viscosity of oil can be lowered by blending with pure ethanol. To reduce of the high viscosity of vegetable oils, microemulsions with immiscible liquids such as methanol and ethanol, and ionic or non-ionic amphiphiles have been studied (Ramadhas *et al.*, 2004; Mittelbach and Gangl, 2001). Short engine performances of both ionic and non-ionic microemul-

sions of ethanol in soybean oil were nearly as good as that of No. 2 diesel (D2) fuel. All microemulsions with butanol, hexanol, and octanol met the maximum viscosity requirement for D2 fuel. 2-octanol was found to be an effective amphiphile in the micellar solubilization of methanol in triolein and soybean oil.

4.5.5.3 Density

Density is another important property of biofuel. Density is the mass *per* unit volume of any liquid at a given temperature. Specific gravity is the ratio of the density of a liquid to the density of water. Density is important in diesel engine performance, since fuel injection operates on a volume metering system (Song, 2000). Also, the density of the liquid product is required for the estimation of the cetane index (Srivastava and Prasad, 2000). The densities were determined using a density meter at 298 K according to ASTM D5002-94. The density meter was calibrated using reverse osmosis water at room temperature.

4.5.5.4 Cetane Number

The cetane number (CN) is a measure of ignition quality or ignition delay, and is related to the time required for a liquid fuel to ignite after injection into a compression ignition engine. CN is based on two compounds, namely hexadecane with a cetane of 100 and heptamethylnonane with a cetane of 15. The CN scale also shows that straight-chain, saturated hydrocarbons have higher CN compared to branched-chain or aromatic compounds of similar molecular weight and number of carbon atoms. It relates to the ignition delay time of a fuel upon injection into the combustion chamber. The CN is a measure of ignition quality of diesel fuels and high CN implies short ignition delay. The longer the fatty acid carbon chains and the more saturated the molecules, the higher the CN. The CN of biofuel from animal fats is higher than that of vegetable oils. CN is determined from real engine tests. The cetane index (CI) is a calculated value derived from the density and volatility obtained from the boiling characteristics of the fuel. CI usually gives a reasonably close approximation to the real cetane number (Song, 2000).

4.5.5.5 Cloud and Pour Points

Two important parameters for low temperature applications of a fuel are the cloud point (CP) and the pour point (PP). CP is the temperature at which a cloud of crystals first appears in a liquid when cooled under conditions as described in ASTM D2500-91. PP is the temperature at which the amount of wax out of the solution is sufficient to gel the fuel; thus it is the lowest temperature at which the fuel can flow. PP is the lowest temperature at which the oil specimen can still be moved. It

is determined according to ASTM D97-96. These two properties are used to specify the cold temperature usability of a fuel. Two cooling baths with different cooling temperatures were used. Triglycerides have higher CP and PP compared to conventional diesel fuel (Prakash, 1998).

4.5.5.6 Distillation Range

The distillation range of a fuel affects its performance and safety. It is an important criterion for an engine's start and warm up. It is also needed in the estimation of the cetane index. The distillation range of the liquid product is determined by a test method (ASTM D2887-97) that covers the determination of the boiling range distribution of liquid fuels.

When the ASTM D86 procedure was used to distil the vegetable oils, they were cleaved into a two-phase distillate. Preliminary data indicate a complex mixture of products including alkanes, alkenes, and carboxylic compounds (Goering *et al.*, 1982). Typically, it is not possible to distil all of the vegetable oil and some brownish residue remained in the distillation flask. However, the soaps obtained from the vegetable oils can be distilled into hydrocarbon-rich products with higher yields. The findings from distillation ranges of vegetable oils are given in the literature (Barsic and Humke, 1981).

4.5.5.7 Heat of Combustion

The heat of combustion measures the energy content in a fuel. This property is also referred to as the calorific value or heating value. Although the cetane number determines the combustion performance, it is the heating value along with thermodynamic criteria that sets the maximum possible output of power (Song, 2000). The higher heating values (HHVs) of oil samples are measured in a bomb calorimeter according to the ASTM D2015 standard method.

The ultimate analysis of a vegetable oil provides the weight percentages of carbon, hydrogen, and oxygen. The carbon, hydrogen, and oxygen contents of various common vegetable oils are 74.5–78.4, 10.6–12.4, and 10.8–12.0 wt%, respectively. The HHV of vegetable oils (Goering *et al.*, 1982) ranges from 37.27–40.48 MJ/kg. The HHVs of different vegetable oils vary by <9%.

The saponification value (SV) of an oil decreases with increase of its molecular weight. On the other hand, the percentages of carbon and hydrogen in oil increase with decrease in molecular weight. The increase in iodine value (IV) (*i.e.*, carbon–carbon double bond, $-\text{C}=\text{C}-$, content) results in a decrease in the heat content of an oil. Therefore, for calculation of the HHVs (MJ/kg) of vegetable oils, Eq. 4.18 was suggested by Demirbas (1998):

$$\text{HHV} = 49.43 - [0.041(\text{SV}) + 0.015(\text{IV})] \quad (4.18)$$

4.5.5.8 Water Content

The water content of the fuel is required to accurately measure the net volume of actual fuel in sales, taxation, exchanges, and custody transfer (Srivastava and Prasad, 2000). Various methods are used for determination of water content in the oil samples such as evaporation methods, distillation methods, the xylene method, the Karl–Fischer titration method, *etc.* Evaporation methods rely on measuring the mass of water in a known mass of sample. The moisture content is determined by measuring the mass of an oil sample before and after the water is removed by evaporation. Distillation methods are based on direct measurement of the amount of water removed from an oil sample by evaporation. The Karl–Fischer titration is often used for determining the moisture content of oils that have low water contents.

4.5.6 Triglyceride Economy

High petroleum prices demand the study of biofuel production. Lower-cost feedstocks are needed since biodiesel from food-grade oils is not economically competitive with petroleum-based diesel fuel. Inedible plant oils have been found to be promising crude oils for the production of biodiesel.

The cost biofuel and demand of vegetable oils can be reduced by inedible oils and used oils, instead of edible vegetable oil. In the world a large amount of inedible oil plants are available in nature.

Vegetable oil is traditionally used as a natural raw material for linoleum, paint, lacquers, cosmetics, and washing powder additives. In the technical range there is a growing market in the field of lubricants, hydraulic oils, and special applications. The energetic use of pure plant oil in motors is an option to replace fossil fuels. Nowadays the technique is tested and well established. Pure plant oil-fuel has the advantages of low sulfur and aromatics contents, and safer handling. Using cold pressed plant oil instead of fossil diesel, there is a reduction in production of the green house gas CO₂.

Everybody is able to produce his own fuel. The cold-pressing process does not require complicated machinery. The characteristics of this process are low energy requirement without any use of chemical extractive agents.

4.6 Biodiesel

Biodiesel (Greek, bio, life + diesel from Rudolf Diesel) refers to a diesel-equivalent, processed fuel derived from biological sources. Biodiesel fuels are attracting increasing attention worldwide as a blending component or a direct replacement for diesel fuel in vehicle engines. Biodiesel is known as monoalkyl, such as methyl and ethyl, esters of fatty acids (FAME) derived from a renewable

lipid feedstock, such as vegetable oil or animal fat. Biodiesel typically comprises alkyl fatty acid (chain length C_{14} – C_{22}) esters of short-chain alcohols, primarily, methanol, or ethanol.

The scarcity of known petroleum reserves will make renewable energy resources more attractive (Sheehan *et al.*, 1998). The most feasible way to meet this growing demand is by utilizing alternative fuels. Biodiesel is defined as the monoalkyl esters of vegetable oils or animal fats. Biodiesel is the best candidate for diesel fuels in diesel engines. The biggest advantage that biodiesel has over petroleum diesel is its environmental friendliness. Biodiesel burns similarly to petroleum diesel as it concerns regulated pollutants. On the other hand biodiesel probably has better efficiency than gasoline. One such fuel for compression-ignition engines that exhibits great potential is biodiesel. Diesel fuel can also be replaced by biodiesel made from vegetable oils. Biodiesel is now mainly being produced from soybean, rapeseed, and palm oils. The higher heating values of biodiesels are relatively high. The higher heating values of biodiesels (39–41 MJ/kg) are slightly lower than that of gasoline (46 MJ/kg), petrodiesel (43 MJ/kg) or petroleum (42 MJ/kg), but higher than coal (32–37 MJ/kg). Biodiesel is over double the price of petrodiesel. The major economic factor to consider for input costs of biodiesel production is the feedstock, which is about 80% of the total operating cost. The high price of biodiesel is in large part due to the high price of the feedstock. Economic benefits of a biodiesel industry would include value added to the feedstock, an increased number of rural manufacturing jobs, increased income taxes, and investments in plant and equipment. The production and utilization of biodiesel is facilitated firstly through the agricultural policy of subsidizing the cultivation of non-food crops. Secondly, biodiesel is exempt from the oil tax. The European Union accounted for nearly 89% of all biodiesel production worldwide in 2005. By 2010, the United States is expected to become the world's largest single biodiesel market, accounting for roughly 18% of world biodiesel consumption, followed by Germany.

Experts suggest that current oil and gas reserves would suffice to last only a few more decades. To exceed the rising energy demand and decreasing petroleum reserves, fuels such as biodiesel and bioethanol are in the forefront of the alternative technologies. Accordingly, the viable alternative for compression-ignition engines is biodiesel.

It is well known that transport is almost totally dependent on fossil particularly petroleum-based fuels such as gasoline, diesel fuel, liquefied petroleum gas (LPG), and natural gas (NG).

An alternative fuel to petrodiesel must be technically feasible, economically competitive, environmentally acceptable, and easily available. This current alternative diesel fuel can be termed as biodiesel. Biodiesel use may improve emissions levels of some pollutants and deteriorate others. However, for quantifying the effect of biodiesel it is important to take into account several other factors such as raw material, driving cycle, vehicle technology, *etc.* Usage of biodiesel will allow a balance to be sought between agriculture, economic development, and the environment (Meher *et al.*, 2006c).

Environmental and political concerns are generating a growing interest in alternative engine fuels such as biodiesel. Biodiesel is a renewable energy source produced from natural oils and fats, which can be used as a substitute for petroleum diesel without the need for diesel engine modification. In addition to being biodegradable and non-toxic, biodiesel is also essentially free of sulfur and aromatics, producing lower exhaust emissions than conventional gasoline whilst providing similar properties in terms of fuel efficiency. The greatest drawback of using pure vegetable oils as fuels are their high viscosity, although this can be reduced by techniques such as dilution, microemulsification, pyrolysis, or transesterification. Of these processes, the transesterification of vegetable oil triglycerides in supercritical methanol has been shown to be particularly promising, producing high yields of low-viscosity methyl esters without the need of a catalyst. Furthermore, these methyl esters have considerably lower flash points than those of pure vegetable oils.

Biodiesel is a clear amber-yellow liquid with a viscosity similar to petrodiesel, the industry term for diesel produced from petroleum. It can be used as an additive in formulations of diesel to increase the lubricity of pure ultra-low sulfur petrodiesel (ULSD) fuel. Much of the world uses a system known as the “B” factor to state the amount of biodiesel in any fuel mix, in contrast to the “BA” system used for bioalcohol mixes. For example, fuel containing 20% biodiesel is labeled B20. Pure biodiesel is referred to as B100. The common international standard for biodiesel is EN 14214. Biodiesel refers to any diesel-equivalent biofuel usually made from vegetable oils or animal fats. Several different kinds of fuels are called biodiesel: usually biodiesel refers to an ester, or an oxygenate, made from the oil and methanol, but alkane (non-oxygenate) biodiesel, that is, biomass-to-liquid (BTL) fuel is also available. Sometimes even unrefined vegetable oil is called “biodiesel”. Unrefined vegetable oil requires a special engine, and the quality of petrochemical diesel is higher. In contrast, alkane biodiesel is of a higher quality than petrochemical diesel, and is actually added to petro-diesel to improve its quality.

Biodiesel has physical properties very similar to petroleum-derived diesel fuel, but its emission properties are superior. Using biodiesel in a conventional diesel engine substantially reduces emissions of unburned hydrocarbons, carbon monoxide, sulfates, polycyclic aromatic hydrocarbons, nitrated polycyclic aromatic hydrocarbons, and particulate matter. Diesel blends containing up to 20% biodiesel can be used in nearly all diesel-powered equipment, and higher-level blends and pure biodiesel can be used in many engines with little or no modification. Lower-level blends are compatible with most storage and distribution equipments, but special handling is required for higher-level blends.

4.6.1 The History of Biodiesel

The process for making fuel from biomass feedstock used in the 1800s is basically the same as that used today. The history of biodiesel is more political and economical than technological. The early 20th century saw the introduction of gaso-

line-powered automobiles. Oil companies were obliged to refine so much crude oil to supply gasoline that they were left with a surplus of distillate, which is an excellent fuel for diesel engines and much less expensive than vegetable oils. On the other hand, resource depletion has always been a concern with regard to petroleum, and farmers have always sought new markets for their products. Consequently, work has continued on the use of vegetable oils as fuel.

Biodiesel from vegetable oils is not a new process. Conversion of vegetable oils or animal fats to the monoalkyl esters or biodiesel is called as transesterification. Transesterification of triglycerides in oils is not a new process. Transesterification of a vegetable oil was conducted as early as 1853, by scientists E. Duffy and J. Patrick, many years before the first diesel engine became functional. Life for the diesel engine began in 1893 when the famous German inventor Dr. Rudolf Diesel published a paper entitled “The theory and construction of a rational heat engine”. What the paper described was a revolutionary engine in which air would be compressed by a piston to a very high pressure thereby causing a high temperature. Dr. Diesel designed the original diesel engine to run on vegetable oil.

Dr. Diesel was educated at the predecessor school to the Technical University of Munich, Germany. In 1878, he was introduced to the work of Sadi Carnot, who theorized that an engine could achieve much higher efficiency than the steam engines of the day. Diesel sought to apply Carnot’s theory to the internal combustion engine. The efficiency of the Carnot cycle increases with the compression ratio – the ratio of gas volume at full expansion to its volume at full compression. Nicklaus Otto invented an internal combustion engine in 1876 that was the predecessor to the modern gasoline engine. Otto’s engine mixed fuel and air before their introduction to the cylinder, and a flame or spark was used to ignite the fuel-air mixture at the appropriate time. However, air gets hotter as it is compressed, and if the compression ratio is too high, the heat of compression will ignite the fuel prematurely. The low compression ratios needed to prevent premature ignition of the fuel-air mixture limited the efficiency of the Otto engine. Dr. Diesel wanted to build an engine with the highest possible compression ratio. He introduced fuel only when combustion was desired and allowed the fuel to ignite on its own in the hot compressed air. Diesel’s engine achieved efficiency higher than that of the Otto engine and much higher efficiency than that of the steam engine. Diesel received a patent in 1893 and demonstrated a workable engine in 1897. Today, diesel engines are classified as “compression-ignition” engines, and Otto engines are classified as “spark-ignition” engines.

Dr. Diesel’s prime model, a single 3 m iron cylinder with a flywheel at its base, ran on its own power for the first time in Augsburg, Germany on August 10, 1893. In remembrance of this event, August 10 has been declared International Biodiesel Day. Diesel later demonstrated his engine and received the “Grand Prix” (highest prize) at the World Fair in Paris, France in 1900. This engine stood as an example of Diesel’s vision because it was powered by peanut oil, a biofuel, though not strictly biodiesel, since it was not transesterified. He believed that the utilization of a biomass fuel was the real future of his engine. In a 1912 speech, Dr. Diesel said “the use of vegetable oils for engine fuels may seem insignificant today, but such

oils may become, in the course of time, as important as petroleum and the coal-tar products of the present time”.

The use of vegetable oils as alternative renewable fuel competing with petroleum was proposed in the beginning of 1980s. The advantages of vegetable oils as diesel fuel are: liquid nature-portability, ready availability, renewability, higher heat content (about 88% of No. 2 petroleum diesel fuel), lower sulfur content, lower aromatic content, and biodegradability. The energy supply concerns of the 1970s renewed interest in biodiesel, but commercial production did not begin until the late 1990s.

Dr. Diesel believed that engines running on plant oils had potential, and that these oils could one day be as important as petroleum-based fuels. Since the 1980s, biodiesel plants have opened in many European countries, and some cities have run busses on biodiesel, or blends of petro and bio diesels. More recently, Renault and Peugeot have approved the use of biodiesel in some of their truck engines. Recent environmental and domestic economic concerns have prompted resurgence in the use of biodiesel throughout the world. In 1991, The European Community (EC) proposed a 90% tax deduction for the use of biofuels, including biodiesel. Biodiesel plants are now being built by several companies in Europe; each of these plants will produce up to 1.5 million gallons of fuel *per* year. The European Union accounted for nearly 89% of all biodiesel production worldwide in 2005.

4.6.2 Definitions of Biodiesel

Bio-diesel or biodiesel refers to a diesel-equivalent, processed fuel derived from biological sources. Biodiesel is the name for a variety of ester-based oxygenated fuel from renewable biological sources. It can be made from processed organic oils and fats.

Chemically, biodiesel is defined as the monoalkyl esters of long chain fatty acids derived from renewable biolipids. Biodiesel is typically produced through the reaction of a vegetable oil or animal fat with methanol or ethanol in the presence of a catalyst to yield (m)ethyl esters (biodiesel) and glycerin (Demirbas, 2002). Fatty acid (m)ethyl esters or biodiesels are produced from natural oils and fats. Generally, methanol is preferred for transesterification, because it is less expensive than ethanol.

The general definition of biodiesel is as follows: Biodiesel is a domestic, renewable fuel for diesel engines derived from natural oils like soybean oil, and which meets the specifications of ASTM D 6751.

Biodiesel is technically defined by using ASTM D 6751. Biodiesel is a diesel engine fuel comprised of monoalkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100, and meeting the requirements of ASTM D 6751. Biodiesel, defined as the monoalkyl esters of fatty acids derived from vegetable oil or animal fat, in application as an extender for combustion in

CIEs (diesel), has demonstrated a number of promising characteristics, including reduction of exhaust emissions. Chemically, biodiesel is referred to as the monoalkyl-esters especially (m)ethylester of long-chain-fatty acids derived from renewable lipid sources *via* transesterification process.

Biodiesel is a mixture of methyl esters of long chain fatty acids like lauric, palmitic, steric, oleic, *etc.* Typical examples are rapeseed oil, canola oil, soybean oil, sunflower oil, and palm oil and its derivatives from vegetable sources. Beef and sheep tallow and poultry oil from animal sources and cooking oil are also the sources of raw materials. The chemistry of conversion to biodiesel is essentially the same. Oil or fat react with methanol or ethanol in the presence of catalyst sodium hydroxide or potassium hydroxide to form biodiesel, (m)ethylesters, and glycerin. Biodiesel is technically competitive with or offers technical advantages compared to conventional petroleum diesel fuel. The biodiesel esters have been characterized for their physical and fuel properties including density, viscosity, iodine value, acid value, cloud point, pure point, gross heat of combustion, and volatility. The biodiesel fuels produce slightly lower power and torque, and higher fuel consumption than No. 2 diesel fuel. Biodiesel is better than diesel fuel in terms of sulfur content, flash point, aromatic content, and biodegradability. Some technical properties of biodiesels are shown in Table 4.25.

The cost of biodiesels varies depending on the base stock, geographic area, variability in crop production from season to season, the price of the crude petroleum, and other factors. Biodiesel has over double the price of petroleum diesel. The high price of biodiesel is in large part due to the high price of the feedstock. However, biodiesel can be made from other feedstocks, including beef tallow, pork lard, and yellow grease.

Biodiesels are biodegradable and non-toxic, and have significantly fewer emissions than petroleum-based diesel (petro-diesel) when burnt. Biodiesel functions in current diesel engines, and is a possible candidate to replace fossil fuels as the world's primary transport energy source. With a flash point of 433 K, biodiesel is

Table 4.25 Some technical properties of biodiesels

Common name	Bio-diesel or biodiesel
Common chemical name	Fatty acid (m)ethyl ester
Chemical formula range	C ₁₄ – C ₂₄ Methyl esters or C _{15–25} H _{28–48} O ₂
Kinematic viscosity range (mm ² /s, at 313 K)	3.3–5.2
Density range (kg/m ³ , at 288 K)	860–894
Boiling point range (K)	>475
Flash point range (K)	428–453
Distillation range (K)	470–600
Vapor pressure (mm Hg, at 295 K)	<5
Solubility in water	Insoluble in water
Physical appearance	Light to dark yellow, clear liquid
Odor	Light musty/soapy odor
Biodegradability	Higher biodegradable than petroleum diesel
Reactivity	Stable, but avoid strong oxidizing agents

classified as a non-flammable liquid by the Occupational Safety and Health Administration. This property makes a vehicle fueled by pure biodiesel far safer in an accident than one powered by petroleum diesel or the explosively combustible gasoline. Precautions should be taken in very cold climates, where biodiesel may gel at higher temperatures than petroleum diesel.

4.6.3 Biodiesel from Triglycerides via Transesterification

The possibility of using vegetable oils as fuel has been recognized since the beginning of diesel engines. Vegetable oil has too high a viscosity for use in most existing diesel engines as a straight replacement fuel oil. There are a number of ways to reduce vegetable oil's viscosity. Dilution, microemulsification, pyrolysis, and transesterification are the four techniques applied to solve the problems encountered with the high fuel viscosity. One of the most common methods used to reduce oil viscosity in the biodiesel industry is called transesterification. Chemical conversion of the oil to its corresponding fatty ester is called transesterification (Bala, 2005).

Transesterification (also called alcoholysis) is the reaction of a fat or oil triglyceride with an alcohol to form esters and glycerol. Figure 4.11 shows the transesterification reaction of triglycerides. A catalyst is usually used to improve the reaction rate and yield. Because the reaction is reversible, excess alcohol is used to shift the equilibrium to the products side.

Figure 4.12 shows the enzymatic biodiesel production by interesterification with methyl acetate in the presence lipase enzyme as catalyst.

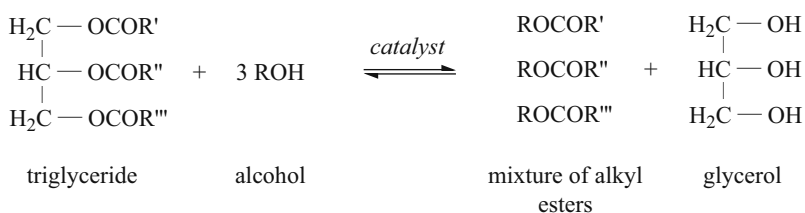


Fig. 4.11 Transesterification of triglycerides with alcohol

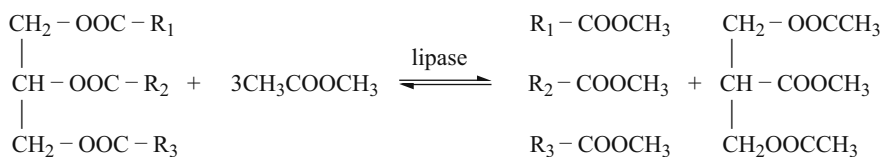


Fig. 4.12 Enzymatic biodiesel production by interesterification with methyl acetate

The biodiesel reaction requires a catalyst such as sodium hydroxide to split the oil molecules and an alcohol (methanol or ethanol) to combine with the separated esters. The main byproduct is glycerin. The process reduces the viscosity of the end product. Transesterification is widely used to reduce vegetable oil viscosity (Pinto *et al.*, 2005). Biodiesel is a renewable fuel source. It can be produced from oil from plants or from animal fats that are byproducts in meat processing.

One popular process for producing biodiesel from the fats/oils is *trans*-esterification of triglyceride by methanol (methanolysis) to make methyl esters of the straight chain fatty acid. The purpose of the transesterification process is to lower the viscosity of the oil. The transesterification reaction proceeds well in the presence of some homogeneous catalysts such as potassium hydroxide (KOH) and sodium hydroxide (NaOH) and sulfuric acid, or heterogeneous catalysts such as metal oxides or carbonates. Sodium hydroxide is very well accepted and widely used because of its low cost and high product yield (Demirbas, 2003a).

Transesterification is the general term used to describe the important class of organic reactions where an ester is transformed into another through interchange of the alkoxy moiety. When the original ester is reacted with an alcohol, the transesterification process is called alcoholysis. In this text, the term transesterification will be used as synonymous for alcoholysis of carboxylic esters, in agreement with most publications in this field. The transesterification is an equilibrium reaction and the transformation occurs essentially by mixing the reactants. However, the presence of a catalyst accelerates considerably the adjustment of the equilibrium. In order to achieve a high yield of the ester, the alcohol has to be used in excess. Transesterification is the process of exchanging the alkoxy group of an ester compound by another alcohol. These reactions are often catalyzed by the addition of a base and acid. Bases can catalyze the reaction by removing a proton from the alcohol, thus making it more reactive, while acids can catalyze the reaction by donating a proton to the carbonyl group, thus making it more reactive. The transesterification reaction proceeds with a catalyst or without any catalyst by using primary or secondary monohydric aliphatic alcohols having 1–8 carbon atoms.

The physical properties of the primary chemical products of transesterification are given in Table 4.26. The high viscosity of the vegetable oils has been the cause of severe operational problems, such as engine deposits. This is a major reason

Table 4.26 Physical properties of chemicals related to transesterification

Name	Specific gravity (g/mL)	Melting point (°C)	Boiling point (°C)	Solubility (<10%)
Methyl myristate	0.875	18.2	–	–
Methyl palmitate	0.825	30.6	196.0	Benzene, EtOH, Et ₂ O
Methyl stearate	0.850	38.0	215.0	Et ₂ O, chloroform
Methyl oleate	0.875	–20.1	190.0	EtOH, Et ₂ O
Methanol	0.792	–104.0	64.7	H ₂ O, ether, EtOH
Ethanol	0.789	–112.0	78.4	H ₂ O, ether
Glycerol	1.260	–18.1	290.0	H ₂ O, ether

Table 4.27 Comparison of various methanolic transesterification methods

Method (min)	Reaction temperature (°C)	Reaction time
Acid or alkali catalytic process	30–35	60–360
Boron trifluoride–methanol	87–117	20–50
Sodium methoxide–catalyzed	20–25	4–6
Non-catalytic supercritical methanol	250–300	6–12
Catalytic supercritical methanol	250–300	0.5–1.5

why neat vegetable oils have largely been abandoned as alternative diesel fuels in favor of monoalkyl esters such as methyl esters. The comparisons various methanolic transesterification methods are tabulated in Table 4.27.

4.6.3.1 Catalytic Transesterification Methods

Vegetable oils can be transesterified by heating them with a large excess of anhydrous methanol and a catalyst. The transesterification reaction can be catalyzed by alkalis (Zhang *et al.*, 2003), acids, or enzymes (Noureddini *et al.*, 2005). Different studies have been carried out using different oils as raw material, different alcohol (methanol, ethanol, butanol), as well as different catalysts, homogeneous ones such as sodium hydroxide, potassium hydroxide, sulfuric acid and supercritical fluids, and heterogeneous ones such as lipases (Bala, 2005).

Sulfuric acid, hydrochloric acid, and sulfonic acid are usually preferred as acid catalysts. The catalyst is dissolved into methanol by vigorous stirring in a small reactor. The oil is transferred into the biodiesel reactor and then the catalyst/alcohol mixture is pumped into the oil.

The transesterification is carried out with the acidic reagent, which is 5% (w/v) anhydrous hydrogen chloride in methanol. It is most often prepared by bubbling hydrogen chloride gas into dry methanol. The hydrogen chloride gas is commercially available in cylinders or can be prepared by dropping concentrated sulfuric acid slowly onto fused ammonium chloride or into concentrated hydrochloric acid. This method is best suited to bulk preparation of the reagent. The hydrogen chloride gas can be obtained by adding acetyl chloride (5 mL) slowly to cooled dry methanol (50 mL).

Vegetable oils are transesterified very rapidly by heating in 10% sulfuric acid in methanol until the reflux. A solution of 1–2% concentrated sulfuric acid in methanol has almost identical properties to 5% methanolic hydrogen chloride, and is very easy to prepare.

Boron trifluoride-catalyzed transesterification of vegetable oils one of the most popular methods. For transesterification of vegetable oils boron trifluoride (BF₃) in methanol (15–20% w/v) is used.

In the alkali catalytic methanol transesterification method, the catalyst (KOH or NaOH) is dissolved into methanol by vigorous stirring in a small reactor. The oil

is transferred into the biodiesel reactor and then the catalyst/alcohol mixture is pumped into the oil. The final mixture is stirred vigorously for 2 hours at 67°C in ambient pressure. A successful transesterification reaction produces two liquid phases: ester and crude glycerin.

The catalyst is dissolved into methanol by vigorous stirring in a small reactor. The oil is transferred into the biodiesel reactor and then the catalyst/alcohol mixture is pumped into the oil. The final mixture is stirred vigorously for 2 hours at 71°C in ambient pressure. A successful transesterification reaction produces two liquid phases: ester and crude glycerin. Crude glycerin, the heavier liquid, will collect at the bottom after several hours of settling. Phase separation can be observed within 10 minutes and can be complete within 2 hours of settling. Complete settling can take as long as 20 hours. After settling is complete, water is added at the rate of 5.5% by volume of the methyl ester of oil and then stirred for 5 minutes, and the glycerin is allowed to settle again. Washing the ester is a two-step process, which is carried out with extreme care. A water wash solution at the rate of 28% by volume of oil and 1 gram of tannic acid *per* liter of water is added to the ester and gently agitated. Air is carefully introduced into the aqueous layer while simultaneously stirring very gently. This process is continued until the ester layer becomes clear. After settling, the aqueous solution is drained and water alone is added at 28% by volume of oil for the final washing (Ma and Hanna, 1999; Demirbas, 2002).

Washing the methyl ester is a two-step process which is carried out with extreme care. A water wash solution at the rate of 28% by volume of oil and 1 g of tannic acid *per* liter of water is added to the methyl ester and gently agitated. Air is carefully introduced into the aqueous layer while simultaneously stirring very gently. This procedure is continued until the methyl ester layer becomes clear. After settling, the aqueous solution is drained and water alone is added at 28% by volume of oil for the final washing. The resulting biodiesel fuel when used directly in a diesel engine will burn up to 75% more cleanly than petroleum No. 2 diesel fuel.

For sodium methoxide-catalyzed transesterification, 100 g of vegetable oil is transesterified in toluene (80 mL) and methanol (200 mL) containing fresh sodium (0.8 g) in 10 minutes at reflux, and a related procedure is used to transesterify liter quantities of oils.

CH_2N_2 reacts rapidly with free fatty acids to give methyl esters. The CH_2N_2 is generally prepared in ethereal solution by the action of alkali (a 30% solution of KOH) on a nitrosamide, *e.g.*, *N*-methyl-*N*-nitroso-*p*-toluene-sulfonamide or nitroso-methyl-urea.

4.6.3.2 Non-catalytic Supercritical Methanol Transesterification

In general, methyl and ethyl alcohols are used in supercritical alcohol transesterification. In the conventional transesterification of animal fats and vegetable oils for biodiesel production, free fatty acids and water always produce negative ef-

fects, since the presence of free fatty acids and water causes soap formation, consumes the catalyst, and reduces catalyst effectiveness, all of which result in a low conversion. The transesterification reaction may be carried out using either basic or acidic catalysts, but these processes are relatively time consuming and complicate separation of the product and the catalyst, which results in high production costs and energy consumption. In order to overcome these problems, Saka and Kusdiana (2001) and Demirbas (2002, 2003a) first proposed that biodiesel fuels may be prepared from vegetable oil *via* non-catalytic transesterification with supercritical methanol (SCM). A novel process of biodiesel fuel production has been developed by a non-catalytic supercritical methanol method. Supercritical methanol is believed to solve the problems associated with the two-phase nature of normal methanol/oil mixtures by forming a single phase as a result of the lower value of the dielectric constant of methanol in the supercritical state. As a result, the reaction was found to be complete in a very short time. Compared with the catalytic processes under barometric pressure, the supercritical methanol process is non-catalytic, purification of products is much simpler, the reaction time is lower, it is more environmentally friendly and uses less energy. However, the reaction requires temperatures of 520–670 K and pressures of 35–60 MPa (Saka and Kusdiana, 2001; Demirbas, 2003a).

The non-catalytic supercritical methanol transesterification is performed in a stainless steel cylindrical reactor (autoclave) at 525 K (Demirbas, 2002). In a typical run, the autoclave is charged with a given amount of vegetable oil and liquid methanol with changed molar ratios. After each run, the gas is vented, and the autoclave is poured into a collecting vessel. The rest of the contents is removed from the autoclave by washing with methanol.

The most important variables affecting the methyl ester yield during transesterification reaction are the molar ratio of alcohol to vegetable oil and the reaction temperature. Viscosities of the methyl esters from vegetable oils were slightly higher than that of No. 2 diesel fuel.

In the transesterification process, the vegetable oil should have an acid value less than 1 and all materials should be substantially anhydrous. If the acid value was greater than 1, more NaOH or KOH was spent to neutralize the free fatty acids. Water also caused soap formation and frothing (Demirbas, 2002).

The stoichiometric ratio for transesterification reaction requires three moles of alcohol and one mole of triglyceride to yield three moles of fatty acid ester and one mole of glycerol. Higher molar ratios result in greater ester production in a shorter time. The vegetable oils were transesterified with 1:6–1:40 vegetable oil–alcohol molar ratios in catalytic and supercritical alcohol conditions (Demirbas, 2002).

Table 4.28 shows critical temperatures and critical pressures of various alcohols. Table 4.29 shows the comparisons between catalytic methanol method and supercritical methanol method for biodiesel from vegetable oils by transesterification. The supercritical methanol process is non-catalytic, simpler purification, has a lower reaction time and lower energy use. Therefore, the supercritical methanol

Table 4.28 Critical temperatures and critical pressures of various alcohols

Alcohol	Critical temperature (K)	Critical pressure (MPa)
Methanol	512.2	8.1
Ethanol	516.2	6.4
1-Propanol	537.2	5.1
1-Butanol	560.2	4.9

Table 4.29 Comparisons between the catalytic methanol (MeOH) method and the supercritical methanol (SCM) method for biodiesel from vegetable oils by transesterification

	Catalytic MeOH process	SCM method
Methylating agent	Methanol	Methanol
Catalyst	Alkali (NaOH or KOH)	None
Reaction temperature (K)	303–338	523–573
Reaction pressure (MPa)	0.1	10–25
Reaction time (min)	60–360	7–15
Methyl ester yield (wt%)	96	98
Removal for purification	Methanol, catalyst, glycerol, soaps	Methanol
Free fatty acids	Saponified products	Methyl esters, water
Exhaust smelling	Soap smelling	Sweet smelling

method should be more effective and efficient than the common commercial process (Kusdiana and Saka, 2004).

The parameters affecting the methyl esters formation are reaction temperature, pressure, molar ratio, water content, and free fatty acid content. It is evident that at the subcritical state of alcohol, the reaction rate is low and gradually increases as either pressure or temperature rises. It was observed that increasing the reaction temperature, especially to supercritical conditions, had a favorable influence on the yield of ester conversion. The yield of alkyl ester increased with increasing the molar ratio of oil to alcohol (Demirbas, 2002). In the supercritical alcohol transesterification method, the yield of conversion rises by 50–95% during the first 10 min. Figure 4.13 shows the plots for changes in fatty acids alkyl esters conversion from triglycerides as treated in supercritical alcohols at 575 K.

Water content is an important factor in the conventional catalytic transesterification of vegetable oil. In the conventional transesterification of fats and vegetable oils for biodiesel production, free fatty acids and water always produce negative effects since the presence of free fatty acids and water causes soap formation, consumes the catalyst, and reduces catalyst effectiveness. In catalyzed methods, the presence of water has negative effects on the yields of methyl esters. However, the presence of water affected positively the formation of methyl esters in our supercritical methanol method. Figure 4.14 shows the plots for yields of methyl esters as a function of water content in transesterification of triglycerides. Figure 4.15 shows the plots for yields of methyl esters as a function of free fatty acid content in biodiesel production.

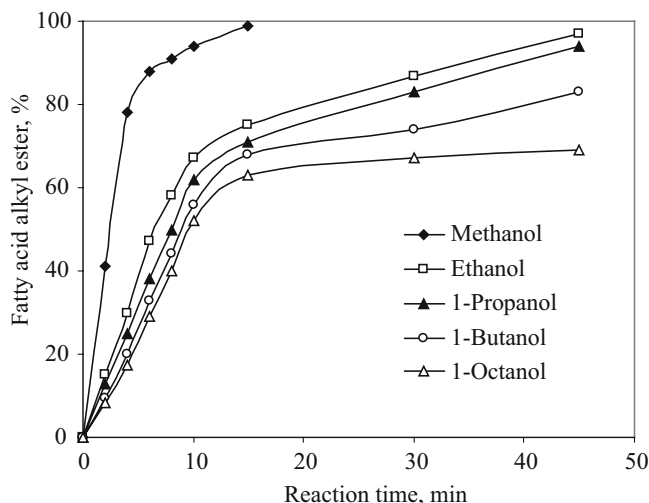


Fig. 4.13 Plots for changes in fatty acids alkyl esters conversion from triglycerides as treated in supercritical alcohols at 575 K

Source: Demirbas, 2008

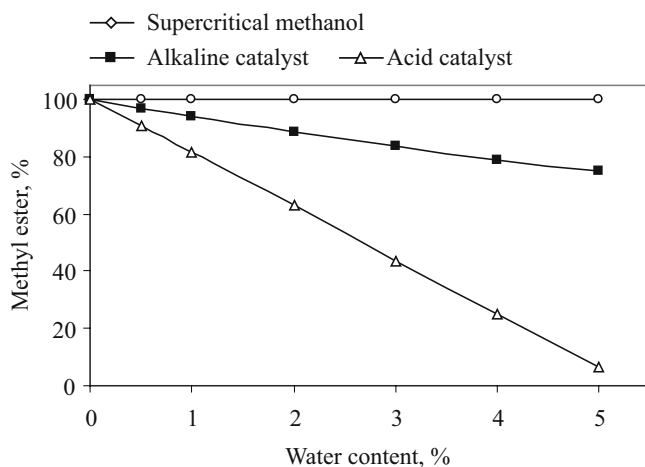


Fig. 4.14 Plots for yields of methyl esters as a function of water content in transesterification of triglycerides

Source: Demirbas, 2008

Figure 4.16 shows the effect of molar ratio of sunflower seed oil to ethanol on yield of ethyl ester at 518 K. The sunflower seed oil was transesterified with 1:1, 1:3, 1:9, 1:20, and 1:40 vegetable oil-ethanol molar ratios in supercritical ethanol conditions. It was observed that an increasing molar ratio had a favorable influence on ester conversion.

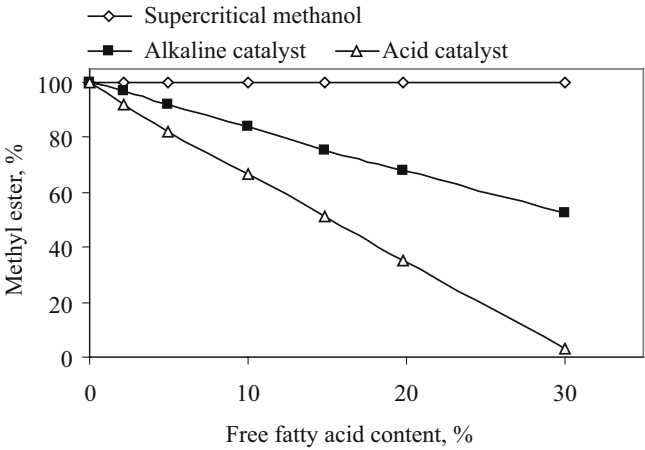


Fig. 4.15 Plots for yields of methyl esters as a function of free fatty acid content in biodiesel production
Source: Demirbas, 2008

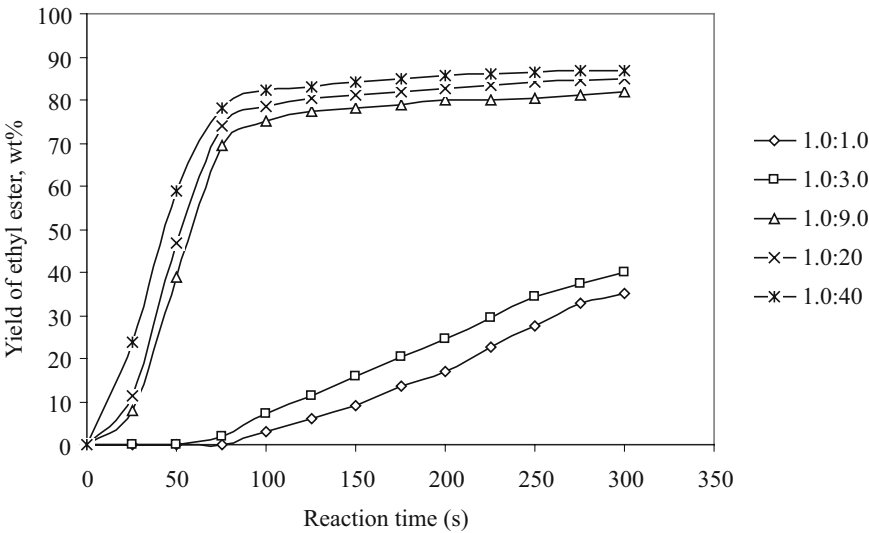


Fig. 4.16 Effects of the molar ratio of vegetable oil to ethanol on yield of ethyl ester. Temperature: 518 K
Source: Balat, 2005

Ethyl esters of vegetable oils have several outstanding advantages among other new-renewable and clean engine fuel alternatives. The variables affecting the ethyl ester yield during transesterification reaction, such as molar ratio of alcohol to vegetable oil and reaction temperature have been investigated. Viscosities of the ethyl esters from vegetable oils were twice as high as that of No. 2 diesel fuel (Balat, 2005).

Catalytic supercritical methanol transesterification is carried out in the autoclave in the presence of 1–5% NaOH, CaO and MgO as a catalyst at 423 K. In the catalytic supercritical methanol transesterification method, the yield of conversion rises 60–90% during the first minute.

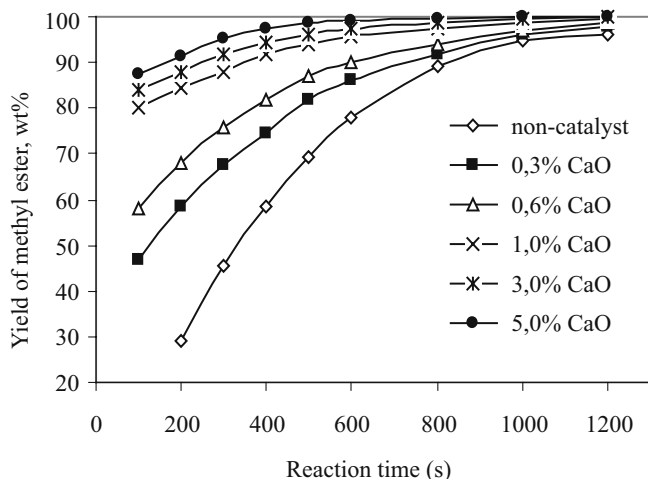


Fig. 4.17 Effect of the CaO content on the methyl ester yield. Temperature: 523 K, molar ratio of methanol to sunflower oil: 41:1

Source: Demirbas, 2008

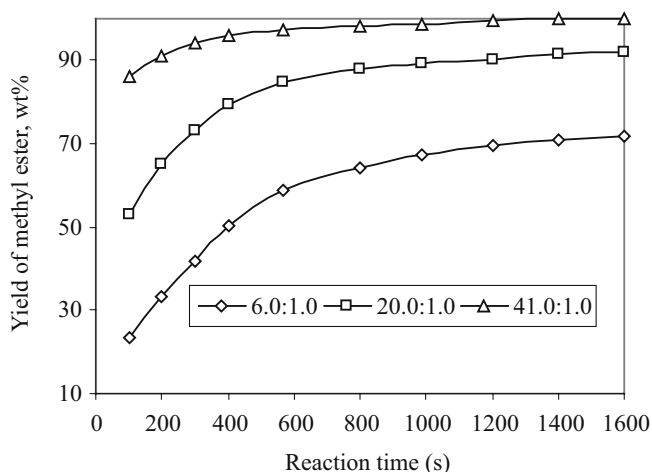


Fig. 4.18 Effect of the molar ratio of methanol to sunflower oil on the methyl ester yield for catalytic (3% CaO) transesterification in supercritical methanol at 523 K

Source: Demirbas, 2008

Figure 4.17 shows the relationship between the reaction time and the catalyst content. It can be affirmed that CaO can accelerate the methyl ester conversion from sunflower oil in 423 K and 24 MPa even if a little catalyst (0.3% of the oil) is added. The transesterification speed obviously improved as the content of CaO increased from 0.3% to 3%. However, when the catalyst content was further enhanced to 5% there was a small increase in the methyl ester yield.

Biodiesel can be obtained from biocatalytic transesterification methods (Noureddini *et al.*, 2005). Methyl acetate, a novel acyl acceptor for biodiesel production has been developed, and a comparative study on Novozym 435-catalyzed transesterification of soybean oil for biodiesel production with different acyl acceptors has been studied (Noureddini *et al.*, 2005). Figure 4.18 shows the effect of the molar ratio of methanol to sunflower oil on the methyl ester yield for catalytic (3% CaO) transesterification in supercritical methanol at 523 K.

4.6.4 Recovery of Glycerol

Glycerol is a byproduct from biodiesel and soap industries. The principal byproduct of biodiesel production is crude glycerol, which is about 10%wt of vegetable oil. Glycerol is the inevitable byproduct of the transesterification process. Direct addition of glycerol to the fuel is not possible. However, derivatives of glycerol such as ethers have potential for use as additives with biodiesel, diesel, or biodiesel-diesel blends. Glycerol can be converted into commercially valued oxygenate products using for the diesel fuel blends. Glycerol alkyl ethers (GAEs) are easily synthesized using glycerol, which is reacted with isobutylene in the presence of an acid catalyst. Etherification of glycerol with isobutylene can be effectively accomplished using Amberlyst-15 as catalyst under a variety of reaction conditions. The ethers of glycerol can be effectively added to biodiesel fuels, providing a 5 K reduction in the cloud point and an 8% reduction in viscosity.

The standards make sure that the following important factors in the biodiesel production process by transesterification are satisfied: (a) complete transesterification reaction, (b) removal of the catalyst, (c) removal of alcohol, (d) removal of glycerol, and (e) complete esterification of free fatty acids. The following transesterification procedure is for methyl ester production. The catalyst is dissolved into the alcohol by vigorous stirring in a small reactor. The oil is transferred into the biodiesel reactor and then the catalyst/methanol mixture is pumped into the oil and final mixture stirred vigorously for two hours. A successful reaction produces two liquid phases: ester and crude glycerol. The entire mixture then settles and glycerol is left on the bottom and methyl esters (biodiesel) are left on top. Crude glycerol, the heavier liquid, will collect at the bottom after several hours of settling. Phase separation can be observed within 10 minutes and can be complete within two hours after stirring has stopped. Complete settling can be taken as long as 18 hours. After settling is complete, water was added at the rate of 5.0% by volume of the oil and then stirred for 5 minutes, and the glycerol allowed to settle

again. After settling is complete the glycerol is drained and the ester layer remains (Bala, 2005).

The recovery of high quality glycerol as a biodiesel byproduct is primary options to be considered to lower the cost of biodiesel. With neutralizing the free fatty acids, removing the glycerol, and creating an alcohol ester transesterification occurs. This is accomplished by mixing methanol with sodium hydroxide to make sodium methoxide. This dangerous liquid is then mixed into vegetable oil. Washing the methyl ester is a two-step process, which is carried out with extreme care. This procedure is continued until the methyl ester layer becomes clear. After settling, the aqueous solution is drained and water alone is added at 28% by volume of oil for the final washing. The resulting biodiesel fuel when used directly in a diesel engine will burn up to 75% cleaner than No. 2 diesel fuel (Bala, 2005).

The process of converting vegetable oil into biodiesel fuel is called transesterification and is luckily less complex than it sounds. Chemically, transesterification means taking a triglyceride molecule or a complex fatty acid, neutralizing the free fatty acids, removing the glycerin, and creating an alcohol ester. This is accomplished by

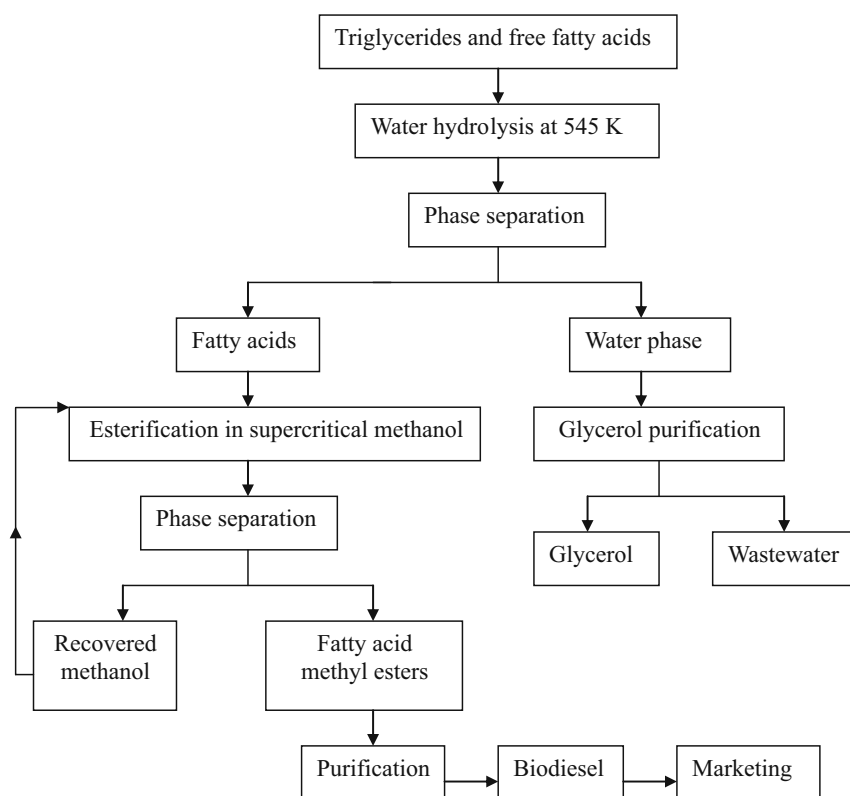
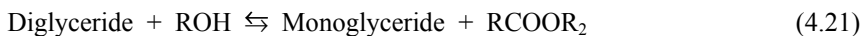
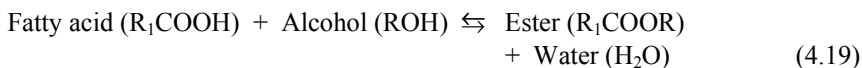


Fig. 4.19 Simple flow diagram of glycerol from continuous biodiesel production process with subcritical water and supercritical methanol stages

mixing methanol with sodium hydroxide to make sodium methoxide. This dangerous liquid is then mixed into vegetable oil. The entire mixture then settles. Glycerin is left on the bottom and methyl esters, or biodiesel, is left on top. The glycerin can be used to make soap (or any one of 1,600 other products) and the methyl esters are washed and filtered. The resulting biodiesel fuel when used directly in a diesel engine will burn up to 75% cleaner than petroleum No. 2 diesel fuel. The recovery of high quality glycerol as a biodiesel byproduct is primary options to be considered to lower the cost of biodiesel. Figure 4.19 shows a flow diagram of glycerol from continuous biodiesel production process with subcritical water and supercritical methanol stages.

4.6.5 Reaction Mechanism of Transesterification

Triacylglycerols (vegetable oils and fats) are esters of long-chain carboxylic acids combined with glycerol. Carboxylic acids $\{R-C(=O)-O-H\}$ can be converted to methyl esters $\{R-C(=O)-O-CH_3\}$ by the action of the transesterification agent. The parameters affecting the methyl esters formation are reaction temperature, pressure, molar ratio, water content, and free fatty acid content. It has been observed that increasing the reaction temperature, has a favorable influence on the yield of ester conversion. The yield of alkyl ester increases with increasing the molar ratio of oil to alcohol (Demirbas, 2002).



Transesterification consists of a number of consecutive, reversible reactions. The triglyceride is converted stepwise to diglyceride, monoglyceride and finally glycerol (Eqs. 4.19–4.22), in which 1 mol of alkyl esters is removed in each step. The reaction mechanism for alkali-catalyzed transesterification was formulated as three steps. The formation of alkyl esters from monoglycerides is believed to be a step that determines the reaction rate, since monoglycerides are the most stable intermediate compound (Ma and Hanna, 1999).

Several aspects, including the type of catalyst (alkaline, acid or enzyme), alcohol/vegetable oil molar ratio, temperature, purity of the reactants (mainly water content) and free fatty acid content have an influence on the course of the transesterification. In the conventional transesterification of fats and vegetable oils for biodiesel production, free fatty acid and water always produce negative effects, since the presence of free fatty acids and water causes soap formation, consumes the catalyst, and reduces catalyst effectiveness, all of which result in a low conversion (Kusdiana and Saka, 2004).

Transesterification is the general term used to describe the important class of organic reactions where an ester is transformed into another through interchange of the alkoxy moiety. When the original ester is reacted with an alcohol, the transesterification process is called alcoholysis. The transesterification is an equilibrium reaction and the transformation occurs essentially by mixing the reactants. In the transesterification of vegetable oils, a triglyceride reacts with an alcohol in the presence of a strong acid or base, producing a mixture of fatty acids alkyl esters and glycerol. The stoichiometric reaction requires 1 mol of a triglyceride and 3 mol of the alcohol. However, an excess of the alcohol is used to increase the yields of the alkyl esters and to allow their phase separation from the glycerol formed.

The base-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reaction. The first step is the reaction of the base with the alcohol, producing an alkoxide and the protonated catalyst. The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate, from which the alkyl ester and the corresponding anion of the diglyceride are formed. The latter deprotonates the catalyst, thus regenerating the active species, which is now able to react with a second molecule of the alcohol, starts another catalytic cycle. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol. Alkaline metal alkoxides (as CH_3ONa for the methanolysis) are the most active catalysts, since they give very high yields (>98%) in short reaction times (30 min) even if they are applied at low molar concentrations (0.5 mol%). However, they require the absence of water, which makes them inappropriate for typical industrial processes.

Alkaline metal hydroxides, such as KOH and NaOH, are cheaper than metal alkoxides, but less active. The presence of water gives rise to hydrolysis of some of the produced ester, with consequent soap formation. The undesirable saponification reaction reduces the ester yields and results in making the recovery of the glycerol very difficult due to the formation of emulsions. Potassium carbonate, used in a concentration of 2% or 3 mol% gives high yields of fatty acid alkyl esters and reduces the soap formation.

There are a number of detailed recipes for sodium methoxide-catalyzed transesterification. The methodology can be used on quite a large scale if need be. The reaction between sodium methoxide in methanol and a vegetable oil is very rapid. It has been shown that triglycerides can be completely transesterified in 2–5 minutes at room temperature. The methoxide anion prepared by dissolving the clean metals in anhydrous methanol. Sodium methoxide (0.5–2M) in methanol effects transesterification of triglycerides much more rapidly than other transesterification agents. At equivalent molar concentrations with the same triglyceride samples, potassium methoxide effects complete esterification more quickly than does sodium methoxide. Because of the dangers inherent in handling metallic potassium, which has a very high heat of reaction with methanol, it is preferred to use sodium methoxide in methanol. The reaction is generally slower with alcohols of higher molecular weight. As with acidic catalysis, inert solvents must be added to dissolve simple lipids before methanolysis will proceed.

4.6.5.1 Parameters Affecting the Formation of Methyl Esters

The parameters affecting the formation of methyl esters are reaction temperature, pressure, molar ratio, water content, and free fatty acid content. It is evident that at subcritical state of alcohol, the reaction rate is so low and gradually increases as either pressure or temperature rises. It has been observed that increasing the reaction temperature, especially to supercritical conditions, has a favorable influence on the yield of ester conversion. The yield of alkyl ester increases with increasing the molar ratio of oil to alcohol (Demirbas, 2002). In the supercritical alcohol transesterification method, the yield of conversion raises 50–95% for the first 10 minutes. Figure 4.20 shows the changes in yield percentage of ethyl esters as treated with subcritical and supercritical ethanol at different temperatures as a function of the reaction time.

Water content is an important factor in the conventional catalytic transesterification of vegetable oil. In the conventional transesterification of fats and vegetable oils for biodiesel production, free fatty acids and water always produce negative effects since the presence of free fatty acids and water causes soap formation, consumes the catalyst, and reduces catalyst effectiveness. In catalyzed methods, the presence of water has negative effects on the yields of methyl esters. However, the presence of water affects positively the formation of methyl esters in our supercritical methanol method.

In the supercritical alcohol transesterification method, the yield of conversion increases 50–95% during first 8 minutes. In the catalytic supercritical methanol

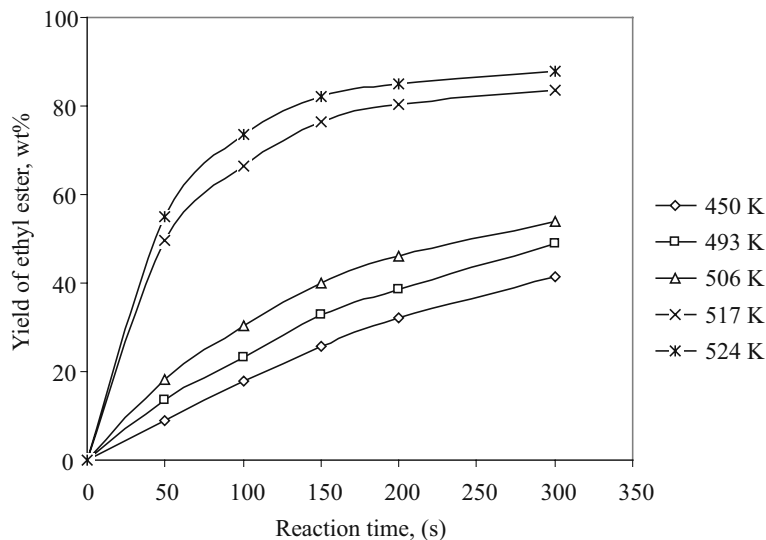


Fig. 4.20 Changes in yield percentage of ethyl esters as treated with subcritical and supercritical ethanol at different temperatures as a function of reaction time. Molar ratio of vegetable oil to ethyl alcohol: 1:40

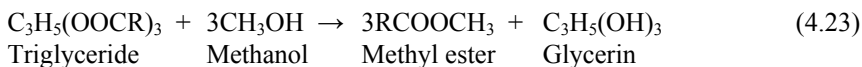
transesterification method, the yield of conversion increases 60–90% during the first minute.

The transesterification can be carried out chemically or enzymatically. In recent work, three different lipases (*Chromobacterium viscosum*, *Candida rugosa*, and Porcine pancreas) were screened for a transesterification reaction of *Jatropha* oil in a solvent-free system to produce biodiesel; only lipase from *Chromobacterium viscosum* was found to give an appreciable yield (Shah *et al.*, 2004). Immobilization of lipase (*Chromobacterium viscosum*) on Celite-545 enhanced the biodiesel yield to 71% from 62% yield obtained by using free tuned enzyme preparation with a process time of 8 h at 113 K. Immobilized *Chromobacterium viscosum* lipase can be used for ethanolysis of oil. It was seen that immobilization of lipases and optimization of transesterification conditions resulted in adequate yield of biodiesel in the case of the enzyme-based process (Shah *et al.*, 2004).

Although the enzyme-catalyzed transesterification processes are not yet commercially developed, new results have been reported in recent articles and patents. The common aspects of these studies consist in optimizing the reaction conditions (solvent, temperature, pH, type of microorganism that generates the enzyme, *etc.*) in order to establish suitable characteristics for an industrial application. However, the reaction yields as well as the reaction times are still unfavorable compared to the base-catalyzed reaction systems. Due to their ready availability and the ease with which they can be handled, hydrolytic enzymes have been widely applied in organic synthesis.

4.6.6 Current Biodiesel Production Technologies

Transesterification is basically a sequential reaction. Triglycerides are first reduced to diglycerides during the transesterification. The diglycerides are subsequently reduced to monoglycerides. The monoglycerides are finally reduced to fatty acid esters. The order of the reaction changes with the reaction conditions. Transesterification is extremely important for biodiesel. Biodiesel as it is defined today is obtained by transesterifying the triglycerides with methanol. Methanol is the preferred alcohol for obtaining biodiesel because it is the cheapest alcohol. Base catalysts are more effective than acid catalysts and enzymes (Ma and Hanna, 1999). Methanol is made to react with the triglycerides to produce methyl esters (biodiesel) and glycerol (Eq. 4.23).



The production processes for biodiesel are well known. There are four basic routes to biodiesel production from oils and fats: (a) base catalyzed transesterification, (b) direct acid catalyzed transesterification, (c) conversion of the oil to its fatty acids and then to biodiesel, and (d) non-catalytic transesterification of oils and fats.

The basic catalyst is typically sodium hydroxide (caustic soda) or potassium hydroxide (caustic potash). It is dissolved in the alcohol using a standard agitator or mixer. The methyl alcohol and catalyst mix is then charged into a closed reactor and the oil or fat is added. The reaction mix is kept just above the boiling point of the alcohol (around 344 K) to speed up the reaction and the transesterification reaction takes place. Recommended reaction time varies from 1 to 8 hours, and the optimal reaction time is about 2 hours (Van Gerpen *et al.*, 2004). Excess alcohol is normally used to ensure total conversion of the fat or oil to its esters. After the reaction is complete, two major products form: glycerin and biodiesel. Each has a substantial amount of the excess methanol that was used in the reaction. The reacted mixture is sometimes neutralized at this step if needed. The glycerin phase is much denser than biodiesel phase, and the two can be gravity separated with glycerin simply drawn off the bottom of the settling vessel. In some cases, a centrifuge is used to separate the two materials faster. The biodiesel product is sometimes purified by washing gently with warm water to remove residual catalyst or soaps, dried, and sent to storage (Ma and Hanna, 1999; Demirbas, 2002). For an alkali-catalyzed transesterification, the triglycerides and alcohol must be substantially anhydrous because water makes the reaction partially change to saponification, which produces soap. The soap lowers the yield of esters and renders the separation of ester and glycerol and the water washing difficult. Low free fatty acid content in triglycerides is required for alkali-catalyzed transesterification. If more water and free fatty acids are in the triglycerides, acid catalyzed transesterification can be used.

When an alkali catalyst is present, the free fatty acid will react with alkali catalyst to form soap. It is common for oils and fats to contain small amounts of water. When water is present in the reaction it generally manifests itself through excessive soap production. The soaps of saturated fatty acids tend to solidify at ambient temperatures so a reaction mixture with excessive soap may gel and form a semi-solid mass that is very difficult to recover. When water is present, particularly at high temperatures, it can hydrolyze the triglycerides to diglycerides and form a free fatty acid.

If an oil or fat containing a free fatty acid such as oleic acid is used to produce biodiesel, the alkali catalyst typically used to encourage the reaction will react with this acid to form soap. This reaction is undesirable because it binds the catalyst into a form that does not contribute to accelerating the reaction. Excessive soap in the products can inhibit later processing of the biodiesel, including glycerol separation and water washing. Water in the oil or fat can also be problem (Van Gerpen *et al.*, 2004).

In some systems the biodiesel is distilled in an additional step to remove small amounts of color bodies to produce a colorless biodiesel. Once the glycerin and biodiesel phases have been separated, the excess alcohol in each phase is removed with a flash evaporation process or by distillation. The glycerin byproduct contains unused catalyst and soaps that are neutralized with sulfuric acid and sent to storage as crude glycerin. In most cases the salt is left in the glycerin. Water and alcohol are removed to produce 90% pure glycerin that is ready to be sold as crude glycerin. Before to use as a commercial fuel, the finished biodiesel must be analyzed using sophisticated analytical equipment to ensure it meets ASTM specifications.

The primary raw materials used in the production of biodiesel are vegetable oils, animal fats, and recycled greases. These materials contain triglycerides, free fatty acids, and other impurities. The primary alcohol used to form the ester is the other major feedstock. Most processes for making biodiesel use a catalyst to initiate the esterification reaction. The catalyst is required because the alcohol is sparingly soluble in the oil phase. The catalyst promotes an increase in solubility to allow the reaction to proceed at a reasonable rate. The most common catalysts used are strong mineral bases such as sodium hydroxide and potassium hydroxide. After the reaction, the base catalyst must be neutralized with a strong mineral acid. Figure 4.21 shows the simplified flow diagram of base catalyzed biodiesel processing.

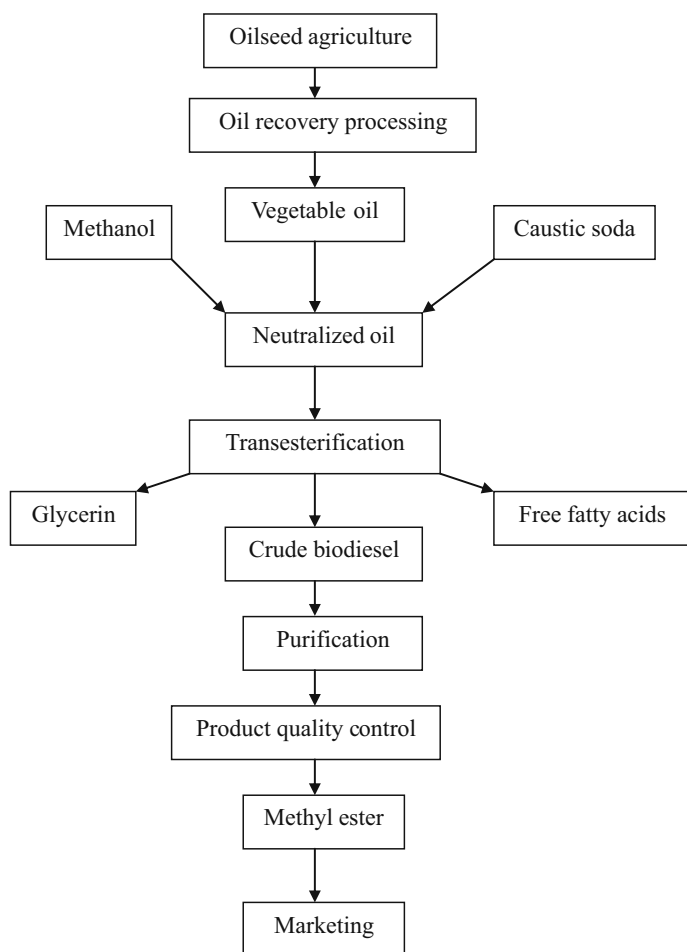
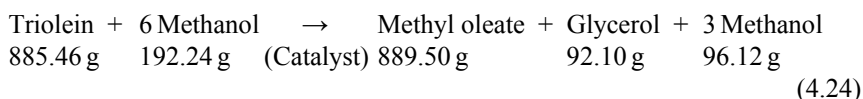


Fig. 4.21 Simplified flow diagram of base catalyzed biodiesel processing

Table 4.30 shows the typical proportions for the chemicals used to make biodiesel. The quantitized transesterification reaction of triolein obtained for methyl oleate (biodiesel) is given in Eq. 4.24.



The most important aspects of biodiesel production to ensure trouble free operation in diesel engines are:

- Complete transesterification reaction
- Removal of glycerol
- Removal of catalyst
- Removal of alcohol
- Removal of free fatty acids.

These parameters are all specified through the biodiesel standard, ASTM D 6751. This standard identifies the parameters the pure biodiesel (B100) must meet before being used as a pure fuel or being blended with petroleum-based diesel fuel. Biodiesel, B100, specifications (ASTM D 6751–02 requirements) are tabulated in Table 4.31.

Table 4.30 Typical proportions of the chemicals used to make biodiesel

Reactants	Amount (kg)
Fat or oil	100
Primary alcohol (methanol)	10
Catalyst (sodium hydroxide)	0.30
Neutralizer (sulfuric acid)	0.36

Table 4.31 Biodiesel, B100, specifications (ASTM D 6751-02 requirements)

Property	Method	Limits	Units
Flash point	D 93	130 min	K
Water and sediment	D 2709	0.050 max	% volume
Kinematic viscosity at 313 K	D 445	1.9–6.0	mm ² /s
Sulfated ash	D 874	0.020 max	wt%
Total sulfur	D 5453	0.05 max	wt%
Copper strip corrosion	D 130	No. 3 max	–
Cetane number	D 613	47 min	–
Cloud point	D 2500	Report	K
Carbon residue	D 4530	0.050 max	wt%
Acid number	D 664	0.80 max	mg KOH/g
Free glycerin	D 6584	0.020	wt%
Total glycerin	D 6584	0.240	wt%
Phosphorus	D 4951	0.0010	wt%
Vacuum distillation end point	D 1160	633 K max, at 90% distilled	K

Table 4.32 International standard (EN 14214) requirements for biodiesel

Property	Units	Lower limit	Upper limit	Test-Method
Ester content	% (m/m)	96.5	–	Pr EN 14103d
Density at 288 K	kg/m ³	860	900	EN ISO 3675/ EN ISO 12185
Viscosity at 313 K	mm ² /s	3.5	5.0	EN ISO 3104
Flash point	K	>374	–	ISO CD 3679e
Sulfur content	mg/kg	–	10	–
Tar remnant (at 10% distillation remnant)	% (m/m)	–	0.3	EN ISO 10370
Cetane number	–	51.0	–	EN ISO 5165
Sulfated ash content	% (m/m)	–	0.02	ISO 3987
Water content	mg/kg	–	500	EN ISO 12937
Total contamination	mg/kg	–	24	EN 12662
Copper band corrosion (3 hours at 323 K)	rating	Class 1	Class 1	EN ISO 2160
Oxidation stability, 383 K	hours	6	–	pr EN 14112k
Acid value	mg KOH/g	–	0.5	pr EN 14104
Iodine value	–	–	120	pr EN 14111
Linoleic acid methyl ester	% (m/m)	–	12	pr EN 14103d
Polyunsaturated (≥ 4 double bonds) methylester	% (m/m)	–	1	–
Methanol content	% (m/m)	–	0.2	pr EN 141101
Monoglyceride content	% (m/m)	–	0.8	pr EN 14105m
Diglyceride content	% (m/m)	–	0.2	pr EN 14105m
Triglyceride content	% (m/m)	–	0.2	pr EN 14105m
Free glycerine	% (m/m)	–	0.02	pr EN 14105m/ pr EN 14106
Total glycerine	% (m/m)	–	0.25	pr EN 14105m
Alkali metals (Na+K)	mg/kg	–	5	pr EN 14108/ pr EN 14109
Phosphorus content	mg/kg	–	10	pr EN14107p

EN 14214 is an international standard that describes the minimum requirements for biodiesel that has been produced from rapeseed fuel stock (also known as rapeseed methyl esters). Table 4.32 shows international standard (EN 14214) requirements for biodiesel.

4.6.7 Biodiesel Production Processes

The main factors affecting transesterification are the molar ratio of glycerides to alcohol, catalyst, reaction temperature and pressure, reaction time, and the contents of free fatty acids and water in oils. The choice of oils or fats to be used in producing biodiesel is an important aspect of economic decision. The cost of oils

or fats directly affects on the cost of biodiesel cost by 70–80%. Crude vegetable oils contain some free fatty acids and phospholipids. The phospholipids are removed in a *degumming* step, and the free fatty acids are removed in a *refining* step. Excess free fatty acids can be removed as soaps in a later transesterification or caustic stripping step.

The most desirable vegetable oils sources are soybean, canola, palm, and rape. Main animal fat sources are beef tallow, lard, poultry fat, and fish oils. Yellow greases can be mixtures of vegetable and animal sources. The free fatty acid content affects the type of biodiesel process used, and the yield of fuel from that process. Other contaminants present can affect the extent of feedstock preparation necessary to use a given reaction chemistry.

From the viewpoint of chemical reaction, refined vegetable oil is the best starting material to produce biodiesel because the conversion of pure triglyceride to fatty acid methyl ester is high, and the reaction time is relatively short. Nevertheless, waste cooking oil, if no suitable treatment is available, would be discharged and cause environmental pollution, but waste cooking oil can be collected for further purification and then biodiesel processing. This collected material is a good commercial choice to produce biodiesel due to its low cost (Zhang *et al.*, 2003).

The most commonly used primary alcohol used in biodiesel production is methanol, although other alcohols, such as ethanol, isopropanol, and butyl, can be used. A key quality factor for the primary alcohol is the water content. Water interferes with transesterification reactions and can result in poor yields and high levels of soap, free fatty acids, and triglycerides in the final fuel.

The stoichiometric ratio for transesterification reaction requires three moles of alcohol and one mole of triglyceride to yield three moles of fatty acid ester and one mole of glycerol. Higher molar ratios result in greater ester production in a shorter time. The commonly accepted molar ratios of alcohol to vegetable oils are 3:1–6:1. Excess methanol (such as the 21:1 ratio) is generally necessary in batch reactors where water accumulates. Another method is to approach the reaction in two stages: fresh methanol and sulfuric acid is reacted, removed, and replaced with fresher reactant. Much of the water is removed in the first round and the fresh reactant in the second round drives the reaction closer to completion. The reason for using extra alcohol is that it drives the reaction closer to the 99.7% yield needed to meet the total glycerol standard for fuel grade biodiesel. The unused alcohol must be recovered and recycled back into the process to minimize operating costs and environmental impacts (Van Gerpen *et al.*, 2004).

The most commonly used catalyst materials for converting triglycerides to biodiesel are sodium hydroxide, potassium hydroxide, and sodium methoxide. Most base catalyst systems use vegetable oils as a feedstock. The base catalysts are highly hygroscopic and they form chemical water when dissolved in the alcohol reactant. They also absorb water from the air during storage.

Acid catalysts can be used for transesterification, however, they are generally considered to be too slow for industrial processing. Acid catalysts are more com-

monly used for the directly esterification of free fatty acids. Acid catalysts include sulfuric acid and phosphoric acid.

There is continuing interest in using lipases as enzymatic catalysts for the production of alkyl fatty acid esters. Some enzymes work on the triglycerides, converting them to methyl esters; and some work on the fatty acids.

Neutralizers are used to remove the base or acid catalyst from the product biodiesel and glycerol. If a base catalyst is used, the neutralizer is typically an acid, and *visa versa*. If the biodiesel is being washed, the neutralizer can be added to the wash water. While hydrochloric acid is a common choice to neutralize base catalysts, as mentioned earlier, if phosphoric acid is used, the resulting salt has value as a chemical fertilizer.

4.6.7.1 Biodiesel Production with Batch Processing

The simplest method for producing alcohol esters is to use a batch, stirred tank reactor. Alcohol to triglyceride ratios from 4:1–20:1 (mole:mole) have been reported, with a 6:1 ratio being most common. The reactor may be sealed or equipped with a reflux condenser. The operating temperature is usually about 340 K, although temperatures from 298–358 K have been reported (Ma and Hanna, 1999; Demirbas, 2002; Bala, 2005). The most commonly used catalyst is sodium hydroxide, with potassium hydroxide also being used. Typical catalyst loadings range from 0.3% to about 1.5%. Completions of transesterification of 85–95% have been reported. Higher temperatures and higher alcohol:oil ratios also can enhance the percent completion. Typical reaction times range from 20 minutes to more than 1 hour.

The oil is first charged to the system, followed by the catalyst and methanol. The system is agitated during the reaction time. Then agitation is stopped. In some processes, the reaction mixture is allowed to settle in the reactor to give an initial separation of the esters and glycerol. In other processes the reaction mixture is pumped into a settling vessel, or is separated using a centrifuge (Van Gerpen *et al.*, 2004).

The alcohol is removed from both the glycerol and ester stream using an evaporator or a flash unit. The esters are neutralized, washed gently using warm, slightly acid water to remove residual methanol and salts, and then dried. The finished biodiesel is then transferred to storage. The glycerol stream is neutralized and washed with soft water. The glycerol is then sent to the glycerol refining unit.

High free fatty acid feedstocks will react with the catalyst and form soaps if they are fed to a base catalyzed system. The maximum amount of free fatty acids acceptable in a base catalyzed system is less than 2%, and preferably less than 1%.

The Lurgi process is shown as a two-step reactor. Most of the glycerin is recovered after the first stage where a rectifying column leads to separation of the excess methanol and crude glycerin. The methyl ester output of the second stage is purified to some extent of residual glycerin and methanol by a wash column. Table 4.33 shows the inputs and mass requirements for the Lurgi process.

Table 4.33 Inputs and mass requirements for the Lurgi process

Input	Requirement/ton biodiesel
Feedstock	1,000 kg vegetable oil
Steam requirement	415 kg
Electricity	12 kWh
Methanol	96 kg
Catalyst	5 kg
Hydrochloric acid (37%)	10 kg
Caustic soda (50%)	1.5 kg
Nitrogen	1 Nm ³
Process water	20 kg

4.6.7.2 Biodiesel Production with Continuous Processes

Transesterification can be conventionally performed using alkaline, acid, or enzyme catalysts. As alkali-catalyzed systems are very sensitive to both water and free fatty acids contents, the glycerides and alcohol must be substantially anhydrous because water makes the reaction partially change to saponification, which produces soaps, thus consuming the catalyst and reducing the catalytic efficiency, as well as causing an increase in viscosity, formation of gels, and difficulty in separations (Ma and Hana, 1999; Zhang *et al.*, 2003).

There are several processes that use intense mixing, either from pumps or motionless mixers, to initiate the esterification reaction. A popular variation of the batch process is the use of continuous stirred tank reactors in series. Instead of allowing time for the reaction in an agitated tank, the reactor is tubular. The reaction mixture moves through this type of reactor in a continuous plug, with little mixing in the axial direction. The result is a continuous system that requires rather short residence times, as low as 6–10 min, for near completion of the reaction.

4.6.7.3 Biodiesel Production with Non-catalyzed Transesterification

There are two non-catalyzed transesterification processes. These are BIOX co-solvent process and supercritical methanol process.

The BIOX (co-)process is a new Canadian process developed originally by Professor David Boocock of the University of Toronto, which has attracted considerable attention. Dr. Boocock has transformed the production process through the selection of inert co-s that generate an oil-rich one-phase system. This reaction is over 99% complete in seconds at ambient temperatures, compared to previous processes that required several hours. BIOX is a technology development company that is a joint venture of the University of Toronto Innovations Foundation and Madison Ventures Ltd. BIOX's patented production process converts first the free fatty acids (by way of acid esterification) up to 10% FFA content and then the

triglycerides (by way of transesterification), through the addition of a co-solvent, in a two-step, single phase, continuous process at atmospheric pressures and near-ambient temperatures. The co-solvent is then recycled and reused continuously in the process. The unique feature of the BIOX process is that it uses inert reclaimable co-s in a single-pass reaction taking only seconds at ambient temperature and pressure. The developers are aiming to produce biodiesel that is cost competitive with petrodiesel. The BIOX process handles not only grain-based feedstocks but also waste cooking greases and animal fats (Van Gerpen *et al.*, 2004). The BIOX process uses a co-solvent, tetrahydrofuran, to solubilize the methanol. Co-options are designed to overcome slow reaction times caused by the extremely low solubility of the alcohol in the triglyceride phase. The result is a fast reaction, on the order of 5–10 min, and no catalyst residues in either the ester or the glycerol phase.

In the conventional transesterification of animal fats and vegetable oils for biodiesel production, free fatty acids and water always produce negative effects since the presence of free fatty acids and water causes soap formation, consumes the catalyst, and reduces catalyst effectiveness, all of which results in a low conversion. The transesterification reaction may be carried out using either basic or acidic catalysts, but these processes require relatively time-consuming and complicated separation of the product and the catalyst, which results in high production costs and energy consumption. To overcome these problems, Kusdiana and Saka (2001) and Demirbas (2002) have proposed that biodiesel fuels may be prepared from vegetable oil *via* non-catalytic transesterification with supercritical methanol (SCM). A novel process of biodiesel fuel production has been developed by a non-catalytic supercritical methanol method. Supercritical methanol is believed to solve the problems associated with the two-phase nature of normal methanol/oil mixtures by forming a single phase as a result of the lower value of the dielectric constant of methanol in the supercritical state. As a result, the reaction was found to be complete in a very short time. Compared with the catalytic processes under barometric pressure, the supercritical methanol process is non-catalytic, involves a much simpler purification of products, has a lower reaction time, is more environmentally friendly, and requires lower energy use. However, the reaction requires temperatures of 525–675 K and pressures of 35–60 MPa.

The dynamic transesterification reaction of peanut oil in supercritical methanol media has been investigated. The reaction temperature and pressure were in the range of 523–583 K and 10.0–16.0 MPa, respectively. The molar ratio of peanut oil to methanol was 1:30. It was found that the yield of methyl esters was higher than 90% under the supercritical methanol. The apparent reaction order and activation energy of transesterification was 1.5 and 7.472 kJ/mol, respectively. In this method, the reaction time was shorter and the processing was simpler than that of the common acid catalysis transesterification.

Figure 4.22 shows the two-stage continuous biodiesel production process with subcritical water and supercritical methanol. The oil and the alcohol stream are fed into the supercritical reactor at 1 atm and 298 K. In the first stage triglycerides rapidly hydrolyze to free fatty acids under 10 MPa pressure at 445 K temperature in the supercritical reactor 1. Methanol become supercritical at a pressure of 10 pa and

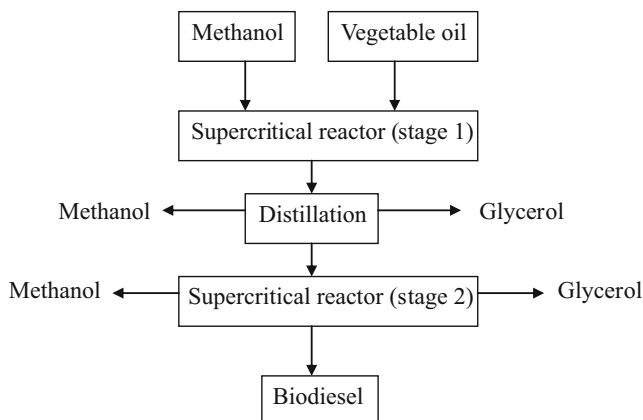


Fig. 4.22 Biodiesel production by supercritical methanol in two stages

a temperature of 445 K, and the supercritical conditions favor rapid formation of methyl esters from the free fatty acids. After the supercritical reactor 1, a distillation column is required to separate the methanol, which will be recycled from the rest. This is done to have a better global separation in the following decanter. When the pressure is reduced the mixture promptly separates into two phases and the water phase can be separated to recover glycerol. In the last equipment, the glycerin is separated from the oil phase; this last one is fed to supercritical reactor 2.

Catalytic supercritical methanol transesterification is carried out in an autoclave in the presence of 1 to 5% NaOH, CaO, and MgO as catalyst at 520 K. In the catalytic supercritical methanol transesterification method, the yield of conversion rises to 60–90% for the first minute. The transesterification reaction of the crude oil of rapeseed with supercritical and subcritical methanol in the presence of a relatively low amount (1%) of NaOH was successfully carried out, where soap formation did not occur.

4.6.8 Basic Plant Equipment Used in Biodiesel Production

The basic plant equipment used in a biodiesel production are reactors, pumps, settling tanks, centrifuges, distillation columns, and storage tanks. The reactor is the only place in the process where chemical conversion occurs. Reactors can be placed into two broad categories, batch reactors and continuous reactors. In the batch reactor, the reactants are charged into the reactor in the determined amount. The reactor is then closed and taken to the desired reaction conditions. The chemical composition within the reactor changes with time. The materials of construction are an important consideration for the reactor and storage tanks. For the base-catalyzed transesterification reaction, stainless steel is the preferred material for the reactor (Van Gerpen *et al.*, 2004).

Key reactor variables that dictate conversion and selectivity are temperature, pressure, reaction time (residence time), and degree of mixing. In general, increasing the reaction temperature increases the reaction rate and, hence, the conversion for a given reaction time. Increasing temperature in the transesterification reaction does impact the operating pressure.

Two reactors within the continuous reactor category are continuous stirred tank reactors (CSTRs) and plug flow reactors (PFRs). For CSTRs, the reactants are fed into a well-mixed reactor. The composition of the product stream is identical to the composition within the reactor. The hold-up time in a CSTR is given by a residence time distribution. For PFRs, the reactants are fed into one side of the reactor. The chemical composition changes as the material moves in plug flow through the reactor (Van Gerpen *et al.*, 2004).

The pumps play the key role in moving chemicals through the manufacturing plant. The most common type of pump in the chemical industry is a centrifugal pump. The primary components of a centrifugal pump are (1) a shaft, (2) a coupling attaching the shaft to a motor, (3) bearings to support the shaft, (4) a seal around the shaft to prevent leakage, (5) an impeller, and (6) a volute, which converts the kinetic energy imparted by the impeller into feet of head. Gear pumps are generally used in biodiesel plants. There are a number of different types of positive displacement pumps, including gear pumps (external and internal) and lobe pumps. External gear pumps generally have two gears with an equal number of teeth located on the outside of the gears, whereas, internal gear pumps have one larger gear with internal teeth and a smaller gear with external teeth (Van Gerpen *et al.*, 2004).

The separation of biodiesel and glycerin can be achieved using a settling tank. While a settling tank may be cheaper, a centrifuge can be used to increase the rate of separation relative to a settling tank. Centrifuges are most typically used to separate solids and liquids, but they can also be used to separate immiscible liquids of different densities. In a centrifuge the separation is accomplished by exposing the mixture to a centrifugal force. The denser phase will be preferentially separated to the outer surface of the centrifuge. The choice of appropriate centrifuge type and size are predicated on the degree of separation needed in a specific system.

An important separation device for miscible fluids with similar boiling points (*e.g.*, methanol and water) is the distillation column. Separation in a distillation column is predicated on the difference in volatilities (boiling points) between chemicals in a liquid mixture. In a distillation column the concentrations of the more volatile species are enriched above the feed point, and the less volatile species are enriched below the feed point.

4.6.9 Fuel Properties of Biodiesels

The fuel properties of biodiesels are characterized by determining their viscosity, density, cetane number, cloud and pour points, distillation range, flash point, ash

content, sulfur content, carbon residue, acid value, copper corrosion, and higher heating value. The most important variables affecting the ester yield during the transesterification reaction are the molar ratio of alcohol to vegetable oil and the reaction temperature. The viscosity values of vegetable oil methyl esters greatly decreases after transesterification process. Compared to No. 2 diesel fuel, all vegetable oil methyl esters are slightly viscous. The flash point values of vegetable oil methyl esters are much lower than those of vegetable oils. The flash point values of vegetable oil methyl esters are much lower than those of vegetable oils. There is a large regression between density and viscosity values vegetable oil methyl esters. The relationships between viscosity and flash point for vegetable oil methyl esters are very regular.

The parameters affecting the formation of methyl esters are reaction temperature, pressure, molar ratio, water content, and free fatty acid content. It is evident that at the subcritical state of alcohol, the reaction rate is very low and gradually increased as either pressure or temperature rises. It has been observed that increasing the reaction temperature, especially to supercritical conditions, has a favorable influence on the yield of ester conversion. The yield of alkyl ester increased with increasing the molar ratio of oil to alcohol.

4.6.9.1 Physical Properties of Biodiesel Fuels

The physical properties and some fuel properties of biodiesel are close to those of diesel fuels. Biodiesel has been characterized by determining its viscosity, density, cetane number, cloud and pour points, characteristics of distillation, flash and combustion points, and higher heating value (HHV) according to ISO norms.

Viscosity is the most important property of biodiesel since it affects the operation of the fuel injection equipment, particularly at low temperatures when the increase in viscosity affects the fluidity of the fuel. High viscosity leads to poorer atomization of the fuel spray and less accurate operation of the fuel injectors. The lower the viscosity of the biodiesel, the easier it is to pump and atomize and achieve finer droplets. The conversion of triglycerides into methyl or ethyl esters through the transesterification process reduces the molecular weight to one-third that of the triglyceride reduces the viscosity by a factor of about 8. Viscosities show the same trends as temperatures, with lard and tallow biodiesels having higher viscosities than soybean and rapeseed biodiesels. Biodiesel has a viscosity close to that of diesel fuels. As the temperature of oil is increase, its viscosity decreases. Table 4.34 shows some fuel properties of six methyl ester biodiesels given by different researchers.

Table 4.35 shows viscosity, density and flash point measurements of nine oil methyl esters. The viscosity, density and flash point values of methyl esters considerably decrease *via* the transesterification process.

Vegetable oils can be used as fuel for combustion engines, but their viscosity is much higher than usual diesel fuel and requires modifications of the engines. The major problem associated with the use of pure vegetable oils as fuels for diesel

Table 4.34 Some fuel properties of six methyl ester biodiesels

Source	Viscosity cSt at 40°C	Density g/mL at 15.5°C	Cetane Number
Sunflower	4.6	0.880	49
Soybean	4.1	0.884	46
Palm	5.7	0.880	62
Peanut	4.9	0.876	54
Babassu	3.6	—	63
Tallow	4.1	0.877	58

Source: Demirbas, 2008

Table 4.35 Viscosity, density and flash point measurements of nine oil methyl esters

Methyl ester	Viscosity mm ² /s (at 313 K)	Density kg/m ³ (at 288 K)	Flash point K
Cottonseed oil	3.75	870	433
Hazelnut kernel oil	3.59	860	422
Linseed oil	3.40	887	447
Mustard oil	4.10	885	441
Palm oil	3.94	880	431
Rapeseed oil	4.60	894	453
Safflower oil	4.03	880	440
Soybean oil	4.08	885	441
Sunflower oil	4.16	880	439

Source: Demirbas, 2008

engines is caused by high fuel viscosity in compression ignition. Therefore, vegetable oils are converted into their methyl esters (biodiesel) by transesterification. The viscosity values of vegetable oils are between 27.2 mm²/s and 53.6 mm²/s, whereas those of vegetable oil methyl esters are between 3.6 mm²/s and 4.6 mm²/s. The viscosity values of vegetable oil methyl esters highly decreases after transesterification process. The viscosity of No. 2 diesel fuel is 2.7 mm²/s at 313 K (Demirbas, 2003a). Compared to No. 2 diesel fuel all of the vegetable oil methyl esters are slightly viscous.

The flash point values of vegetable oil methyl esters are much lower than those of vegetable oils. The flash point values of vegetable oil methyl esters are much lower than those of vegetable oils. An increase in density from 860 kg/m³ to 885 kg/m³ for vegetable oil methyl esters or biodiesels increases the viscosity from 3.59 mm²/s to 4.63 mm²/s and the increases are highly regular. There is high regression between density and viscosity values vegetable oil methyl esters. The relationships between viscosity and flash point for vegetable oil methyl esters are irregular.

The cetane number (CN) is based on two compounds, namely hexadecane with a cetane of 100 and heptamethylnonane with a cetane of 15. CN is a measure of ignition quality of diesel fuels and high CN implies short ignition delay. The CN of CSO samples were the range of 41–44.0. The CN of biodiesel is generally higher than conventional diesel. The longer the fatty acid carbon chains and the more saturated the molecules, the higher the CN. The CN of biodiesel from animal fats is higher than those of vegetable oils (Bala, 2005).

Two important parameters for low temperature applications of a fuel are the cloud point (CP) and the pour point (PP). CP is the temperature at which wax first becomes visible when the fuel is cooled. PP is the temperature at which the amount of wax out of solution is sufficient to gel the fuel, thus it is the lowest temperature at which the fuel can flow. Biodiesel has higher CP and PP compared to conventional diesel.

4.6.9.2 Higher Combustion Efficiency of Biodiesel

Biodiesel is an oxygenated fuel. Oxygen in the biodiesel structure improves its combustion process and decreases its oxidation potential. The structural oxygen content of a fuel improves combustion efficiency due to an increase in the homogeneity of oxygen with the fuel during combustion. Because of this the combustion efficiency of biodiesel is higher than petrodiesel, and the combustion efficiency methanol/ethanol is higher than that of gasoline. A visual inspection of the injector types would indicate no difference between the biodiesel fuels when tested on petrodiesel. The overall injector coking is considerably low. Biodiesel contains 11% oxygen by weight and contains no sulfur. The use of biodiesel can extend the life of diesel engines because it is more lubricating than petroleum diesel fuel. Biodiesel has better lubricant properties than petrodiesel.

The higher heating values of biodiesels are relatively high. The higher heating values (HHVs) of biodiesels (39–41 MJ/kg) are slightly lower than those of gasoline (46 MJ/kg), petrodiesel (43 MJ/kg), or petroleum (42 MJ/kg), but higher than coal (32–37 MJ/kg). Table 4.36 shows a comparison of chemical properties and the HHVs between biodiesel and petrodiesel fuels.

Table 4.36 Comparison of chemical properties and higher heating values (HHVs) between biodiesel and No. 2 diesel fuels

Chemical property	Biodiesel (methyl ester)	No. 2 diesel fuel
Ash (wt%)	0.002–0.036	0.006–0.010
Sulfur (wt%)	0.006–0.020	0.020–0.050
Nitrogen (wt%)	0.002–0.007	0.0001–0.003
Aromatics (vol%)	0	28–38
Iodine number	65–156	0
HHV (MJ/kg)	39.2–40.6	45.1–45.6

Source: Demirbas, 2008

4.6.9.3 Water Content

Water content is an important factor in the conventional catalytic transesterification of vegetable oil. In the conventional transesterification of fats and vegetable oils for biodiesel production, free fatty acids and water always produce negative effects since the presence of free fatty acids and water causes soap formation, consumes the catalyst, and reduces catalyst effectiveness. Soap can prevent the separation of biodiesel from glycerol fraction (Madras *et al.*, 2004). In catalyzed methods, the presence of water has negative effects on the yields of methyl esters. However, the presence of water positively affects the formation of methyl esters in the supercritical methanol method (Kusdiana and Saka, 2004).

4.6.9.4 Comparison of the Fuel Properties of Methyl and Ethyl Alcohols and Their Esters

The main goals of the alcohol studies were to better understand the fuel properties of alcohol and basic principles of conversion in order to provide the representative cross-section of converting diesel engines and gasoline engines to accepting blended fuel.

The alcohols are oxygenated fuels where the alcohol molecule has one or more oxygen atoms, which decreases to the combustion heat. Practically, any of the organic molecules of the alcohol family can be used as a fuel. The alcohols that can be used for motor fuels are methanol, ethanol, propanol, and butanol. However, only two of the alcohols are technically and economically suitable as fuels for internal combustion engines (ICEs). The main production facilities of methanol and ethanol are tabulated in Table 4.37. Methanol is produced by a variety of processes, the most common being the following: distillation of liquid products from wood and coal, natural gas, and petroleum gas. Ethanol is produced mainly from biomass bioconversion (Bala, 2005).

In general, the physical and chemical properties and the performance of ethyl esters are comparable to those of methyl esters. Methyl and ethyl esters have almost the same heat content. The viscosities of ethyl esters are slightly higher and the cloud and pour points are slightly lower than those of methyl esters. Engine tests demonstrated that methyl esters produce slightly higher power and torque than ethyl esters (Encinar *et al.*, 2002). Some desirable attributes of the ethyl esters over methyl esters are: significantly lower smoke opacity, lower exhaust temperatures, and lower pour point. Ethyl esters tend to have more injector coking than methyl esters.

Many alcohols have been used to make biodiesel. Issues such as the cost of the alcohol, the amount of alcohol needed for the reaction, the ease of recovering and recycling the alcohol, fuel tax credits, and global warming issues influence the choice of alcohol. Some alcohols also require slight technical modifications to the production process such as higher operating temperatures, longer or slower mixing times, or lower mixing speeds. Since the reaction to form the esters is on a molar

Table 4.37 Main production facilities of methanol and ethanol for biodiesel production

Product	Production process
Methanol	Distillation of liquid from wood pyrolysis
	Gaseous products from biomass gasification
	Distillation of liquid from coal pyrolysis
	Synthetic gas from biomass and coal
	Natural gas
	Petroleum gas
Ethanol	Fermentation of sugars and starches
	Bioconversion of cellulosic biomass
	Hydration of alkanes
	Synthesis from petroleum
	Synthesis from coal
	Enzymatic conversion of synthetic gas

Source: Demirbas, 2008

basis, and alcohol is purchased on a volume basis, their properties make a significant difference in raw material price. It takes three moles of alcohol to react completely with one mole of triglyceride.

Ethanol is produced a more environmentally benign fuel. The systematic effect of ethyl alcohol differs from that of methyl alcohol. Ethyl alcohol is rapidly oxidized in the body to carbon dioxide and water, and in contrast to methyl alcohol no cumulative effect occurs. Ethanol is also a preferred alcohol in the transesterification process compared to methanol because it is derived from agricultural products and is renewable and biologically less objectionable in the environment. Table 4.37 shows the main production facilities of methanol and ethanol for biodiesel production.

Methanol use in current-technology vehicles has some distinct advantages and disadvantages. On the plus side, methanol has a higher octane rating than gasoline. Methanol vaporizes at such a temperature that it results in lower peak flame temperatures than gasoline and lower nitrogen oxide emissions. Its greater tolerance to lean combustion, higher air-to-fuel equivalence ratio results in generally lower overall emissions and higher energy efficiency. However, several disadvantages must be studied and overcome before neat methanol is considered a viable alternative to gasoline. The energy density of methanol is about half that of gasoline, reducing the range a vehicle can travel on an equivalent tank of fuel.

There are some important differences in the combustion characteristics of alcohols and hydrocarbons. Alcohols have higher flame speeds and extended flammability limits. Pure methanol is very flammable, and its flame is colorless when ignited. The alcohols mix in all proportions with water due to the polar nature of the OH group. Low volatility is indicated by a high boiling point and a high flash point. Combustion of alcohol in the presence of air can be initiated by an inten-

sive source of localized energy, such as a flame or a spark and, also, the mixture can be ignited by application of energy by means of heat and pressure, such as happens in the compression stroke of a piston engine. The high latent heat of vaporization of alcohols cools the air entering the combustion chamber of the engine, thereby increasing the air density and mass flow. This leads to increased volumetric efficiency and reduced compression temperatures. The oxygen contents of alcohols depress the heating value of the fuel in comparison with hydrocarbon fuels. The heat of combustion *per* unit volume of alcohol is approximately half that of isooctane.

Methanol is not miscible with hydrocarbons and separation ensues readily in the presence of small quantities of water, particularly with reduction in temperature. On the other hand, anhydrous ethanol is completely miscible in all proportions with gasoline, although separation may be effected by water addition or by cooling. If water is already present, the water tolerance is higher for ethanol than for methanol, and can be improved by the addition of higher alcohols, such as butanol. Also benzene or acetone can be used. The wear problem is believed to be caused by formic acid attack, when methanol is used or acetic acid attack when ethanol is used.

Methanol is considerably easier to recover than ethanol. Ethanol forms an azeotrope with water, so it is expensive to purify the ethanol during recovery. If the water is not removed it will interfere with the reactions. Methanol recycles more easily because it does not form an azeotrope. These two factors are the reason that even though methanol is more toxic, it is the preferred alcohol for producing biodiesel. Methanol has a flash point of 283 K, while the flash point of ethanol is 281 K, so both are considered highly flammable. One should never let methanol come into contact with skin or eyes, as it can be readily absorbed. Excessive exposure to methanol can cause blindness and other detrimental health effects.

Dry methanol is very corrosive to some aluminum alloys, but additional water at 1% almost completely inhibits corrosion. It must be noted that methanol with additional water at more than 2% becomes corrosive again. Ethanol always contains some acetic acid and is particularly corrosive to aluminum alloys.

Since alcohols, especially methanol, can be readily ignited by hot surfaces, preignition can occur. It must be emphasized here that preignition and knocking in alcohol using engines is a much more dangerous condition than gasoline engines. Other properties, however, are favorable to the increase of power and reduction of fuel consumption. Such properties are as follows: (1) the number of molecules or products is more than that of reactants; (2) extended limits of flammability; (3) high octane number; (4) high latent heat of vaporization; (5) constant boiling temperature; and (6) high density.

Figure 4.23 shows the distillation curves of the No. 2. diesel fuel and linseed oil methyl and ethyl esters. As seen in Fig. 4.23, the most volatile fuel was No. 2. diesel fuel. The volatility of methyl esters was higher than that of ethyl ester at all temperatures.

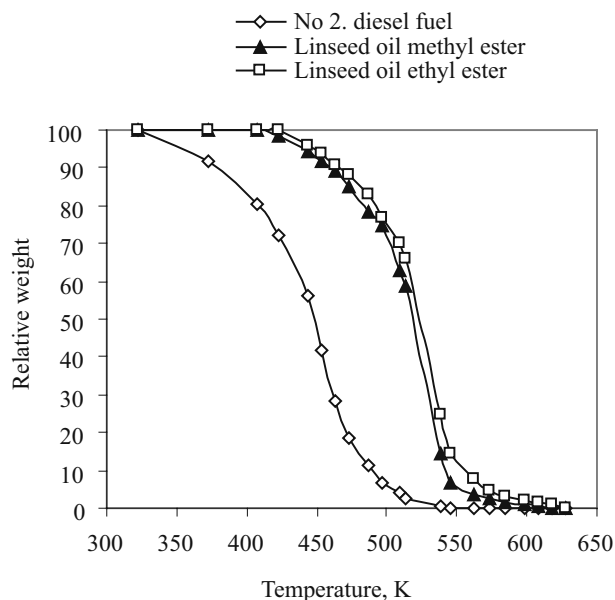


Fig. 4.23 Distillation curves of No 2. diesel fuel and linseed oil methyl and ethyl esters

4.6.10 Advantages of Biodiesels

The advantages of biodiesel as diesel fuel are liquid nature-portability, ready availability, renewability, higher combustion efficiency, lower sulfur and aromatic content (Ma and Hanna, 1999; Knothe *et al.*, 2006), higher cetane number, and higher biodegradability (Zhang *et al.*, 2003). The main advantages of biodiesel given in the literature include domestic origin, reducing the dependency on imported petroleum, biodegradability, high flash point, and inherent lubricity in the neat form (Knothe *et al.*, 2005).

Biodiesel is the only alternative fuel for unmodified conventional diesel engines using low concentration biodiesel-diesel blends. It can be stored anywhere that petroleum diesel fuel is stored. Biodiesel can be made from domestically produced, renewable oilseed crops such as soybean, rapeseed, and sunflower. The risks of handling, transporting, and storing biodiesel are much lower than those associated with petrodiesel. Biodiesel is safe to handle and transport because it is as biodegradable as sugar and has a high flashpoint compared to petroleum diesel fuel. Biodiesel can be used alone or mixed in any ratio with petroleum diesel fuel. The most common blend is a mix of 20% biodiesel with 80% petroleum diesel, or B20 according to recent scientific investigations; however, in Europe the current regulation foresees a maximum 5.75% biodiesel.

Combustion of biodiesel alone provides over a 90% reduction in total unburned hydrocarbons, and a 75–90% reduction in polycyclic aromatic hydrocarbons (PAHs). Biodiesel further provides significant reductions in particulates and carbon monoxide compared to petroleum diesel fuel. Biodiesel provides a slight increase or decrease in nitrogen oxides depending on the engine family and testing procedures.

Fuel characterization data show some similarities and differences between biodiesel and petrodiesel fuels. The sulfur content of petrodiesel is 20–50 times that of biodiesels. Several municipalities are considering mandating the use of low levels of biodiesel in diesel fuel on the basis of several studies that have found hydrocarbon (HC) and particulate matter (PM) benefits from the use of biodiesel.

The use of biodiesel to reduce N_2O is attractive for several reasons. Biodiesel contains little nitrogen, as compared with petrodiesel, which is also used as a re-burning fuel. The N_2O reduction was strongly dependent on initial N_2O concentration and only slightly dependent upon temperature, where increased temperature increased N_2O reduction. This results in lower N_2O production from fuel nitrogen species for biodiesel. In addition, biodiesel contains virtually trace amounts of sulfur, so SO_2 emissions are reduced in direct proportion to the petrodiesel replacement.

Biodiesel has demonstrated a number of promising characteristics, including the reduction of exhaust emissions. Vegetable oil fuels have not been acceptable because they are more expensive than petroleum fuels. With recent increases in petroleum prices and uncertainties concerning petroleum availability, there is renewed interest in vegetable oil fuels for compression ignition (CIE or diesel) engines. Alternative fuels for CIE have become increasingly important due to increased environmental concerns, and several socio-economic aspects. In this sense, vegetable oils and animal fats represent a promising alternative to conventional diesel fuel (Demirbas, 2008).

One of the most common blends of biodiesel contains 20 volume percent biodiesel and 80 volume percent conventional diesel. For soybean-based biodiesel at this concentration, the estimated emission impacts for percent change in emissions of NO_x , PM, HC, and CO were +20%, –10.1%, –21.1%, and –11.0%, respectively (EPA, 2002). The use of blends of biodiesel and diesel oil are preferred in engines, in order to avoid some problems related to the decrease of power and torque and to the increase of NO_x emissions (a contributing factor in the localized formation of smog and ozone) with increasing content of pure biodiesel in the blend. Emissions of all pollutants except NO_x appear to decrease when biodiesel is used. The fact that NO_x emissions increase with increasing biodiesel concentration may be a detriment in areas that are out of attainment for ozone. Figure 4.24 shows the average emission impacts of vegetable oil-based biodiesel for CIE. Figure 4.25 shows average emission impacts of animal-based biodiesel for CIE.

Using biodiesel in a conventional diesel engine substantially reduces emissions of unburned hydrocarbons, carbon dioxide, carbon monoxide, sulfates, polycyclic aromatic hydrocarbons, nitrated polycyclic aromatic hydrocarbons, ozone-forming hydrocarbons, and particulate matter. The net contribution of carbon dioxide from

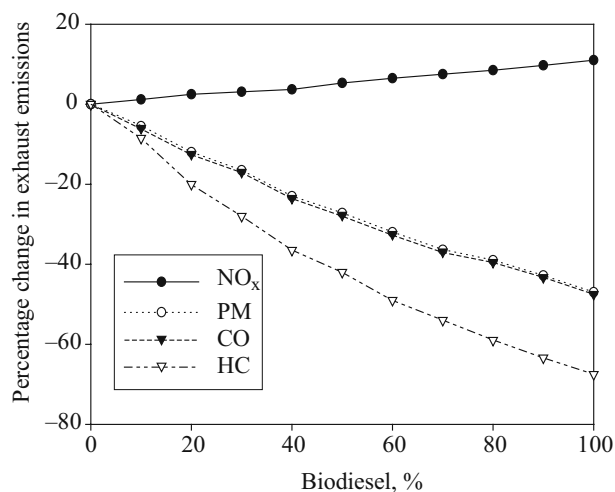


Fig. 4.24 Curves for average emission impacts of vegetable oil-based biodiesel for CIE

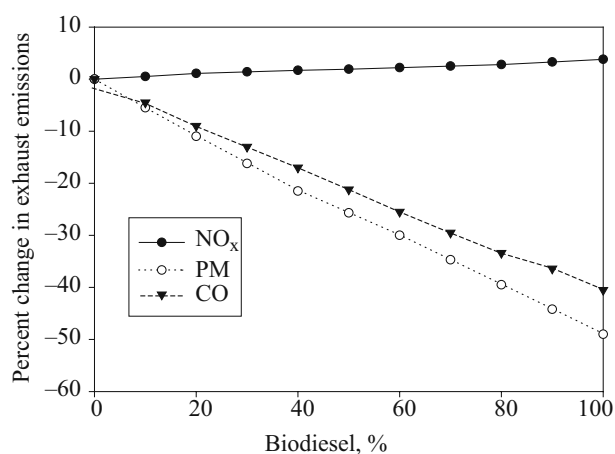


Fig. 4.25 Curves for average emission impacts of animal-based biodiesel for CIE

biomass combustion is small. Reductions in net carbon dioxide emissions are estimated at 77–104 g/MJ of diesel displaced by biodiesel. These reductions increase as the amount of biodiesel blended into diesel fuel increases. The best emissions reductions are seen with biodiesel.

The exhaust emissions of commercial biodiesel and petrodiesel have been studied in a 2003 model year heavy-duty 14 L six-cylinder diesel engine with EGR (Knothe *et al.*, 2006). The commercial biodiesel fuel significantly reduced PM exhaust emissions (75–83%) compared to the petrodiesel base fuel. However, NO_x exhaust emissions were slightly increased with commercial biodiesel compared to

the base fuel. The chain length of the compounds had little effect on NO_x and PM exhaust emissions, while the influence was greater on HC and CO, the latter being reduced with decreasing chain length. Unsaturation in the fatty compounds causes an increase in NO_x exhaust emissions (Knothe *et al.*, 2006).

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Biodiesel fuels can be used as a renewable energy source to substitute conventional petroleum diesel in compression ignition engines. When degradation is caused by biological activity, especially by enzymatic action, it is called biodegradation. Biodegradability of biodiesel has been proposed as a solution for the waste problem. Biodegradable fuels such as biodiesels have an expanding range of potential applications and they are environmentally friendly. Therefore, there is growing interest in degradable diesel fuels that degrade more rapidly than conventional diesel fuels.

The advantages of biodiesel include domestic origin, reducing the dependency on imported petroleum, biodegradability, high flash point, and inherent lubricity in the neat form (Knothe *et al.*, 2005; Mittelbach and Gangl, 2001). Recently, biodiesel has become more attractive because of its environmental benefits and the fact that it is made from renewable resources (Ma and Hanna, 1999).

Biodiesel is non-toxic and degrades about four times faster than petrodiesel. Its oxygen content improves the biodegradation process, leading to a decreased level of quick biodegradation. In comparison with petrodiesel, biodiesel shows better emission parameters. It improves the environmental performance of road transport, including decreased greenhouse emissions (mainly of carbon dioxide).

As biodiesel fuels are becoming commercialized their existence in the environment is an area of concern since petroleum oil spills constitute a major source of contamination of the ecosystem. Among these concerns, water quality is one of the most important issues for living systems. It is important to examine the biodegradability of biodiesel fuels and their biodegradation rates in natural waterways in case they enter the aquatic environment in the course of their use or disposal. Chemicals from biodegradation of biodiesel can be released into the environment. With the increasing interest in biodiesel, the health and safety aspects are of utmost importance, including determination of their environmental impacts in transport, storage, or processing (Ma and Hanna, 1999).

Biodegradation is degradation caused by biological activity, particularly by enzyme action leading to significant changes in the material chemical structure. There are many methods for biodegradation. Among them, the carbon dioxide (CO_2) evolution method is relatively simple, economical, and environmentally

safe. Another method is to measure the biochemical oxygen demand (BOD) with a respirometer (Demirbas, 2008).

The biodegradabilities of several biodiesels in the aquatic environment show that all biodiesel fuels are readily biodegradable. After 28 days all biodiesel fuels were 77–89% biodegraded; diesel fuel was only 18% biodegraded (Zhang, 1996). The enzymes responsible for the dehydrogenation/oxidation reactions that occur in the process of degradation recognize oxygen atoms and attack them immediately (Zhang *et al.*, 1998).

The biodegradability data of petroleum and biofuels available in the literature are presented in Table 4.38. Heavy fuel oil has low biodegradation of 11%, in 28-day laboratory studies, due to its higher proportion of high molecular weight aromatics (Mulkins-Phillips and Stewart, 1974; Walker *et al.*, 1976). Gasoline is less biodegradable (28%) after 28 days. Vegetable oils and their derived methyl esters (biodiesels) are rapidly degraded to reach biodegradation of between 76–90% (Zhang *et al.*, 1998). In their studies Zhang *et al.* (1998) have shown that vegetable oils are slightly less degraded than their modified methyl ester.

Many of the vegetable oils contain polyunsaturated fatty acid chains that are methylene-interrupted rather than conjugated. The double bond of unsaturated fatty acids restricts the rotation of the hydrogen atoms attached to them. Therefore, an unsaturated fatty acid with a double bond can exist in two forms. The *cis* form in which the two hydrogens are on the same “side” and the *trans* form in which the hydrogen atoms are on opposite sides.

Trans unsaturated fatty acids, or *trans* fats, are solid fats produced artificially by heating liquid vegetable oils in the presence of metal catalysts and hydrogen. This process, called partial hydrogenation, causes carbon atoms to bond in a straight configuration and remain in a solid state at room temperature.

Physical properties that are sensitive to the effects of fatty oil oxidation include viscosity, the refractive index, and the di-electric constant. In oxidative instability, the methylene group ($-\text{CH}_2-$) carbons between the olefinic carbons are the sites of first attack.

Oxidation to CO_2 of biodiesel results in the formation of hydroperoxides. The formation of the hydroperoxide follows a well known peroxidation chain mechanism. Oxidative lipid modifications occur through lipid peroxidation mechanisms

Table 4.38 Biodegradability data of petroleum and biofuels

Fuel sample	Degradation in 28 days (%)	References
Gasoline (91 octane)	28	Speidel <i>et al.</i> , 2000
Heavy fuel (Bunker C oil)	11	Mulkins-Phillips and Stewart, 1974; Walker <i>et al.</i> , 1976
Refined rapeseed oil	78	Zhang <i>et al.</i> , 1998
Refined soybean oil	76	Zhang <i>et al.</i> , 1998
Rapeseed oil methyl ester	88	Zhang <i>et al.</i> , 1998
Sunflower seed oil methyl ester	90	Zhang <i>et al.</i> , 1998

in which free radicals and reactive oxygen species abstract a methylene hydrogen atom from polyunsaturated fatty acids, producing a carbon-centered lipid radical. Spontaneous rearrangement of the 1,4-pentadiene yields a conjugated diene, which reacts with molecular oxygen to form a lipid peroxy radical. Abstraction of a proton from neighboring polyunsaturated fatty acids produces a lipid hydroperoxide (LOOH) and regeneration of a carbon-centered lipid radical, thereby propagating the radical reaction. After hydrogen is removed from such carbons oxygen rapidly attacks, and a LOOH is ultimately formed where the polyunsaturation has been isomerized to include a conjugated diene. This reaction is a chain mechanism that can proceed rapidly once an initial induction period has occurred. The greater the level of unsaturation in a fatty oil or ester, the more susceptible it will be to oxidation. Once the LOOHs have formed, they decompose and inter-react to form numerous secondary oxidation products including higher molecular weight oligomers, often called polymers.

4.6.11 Disadvantages of Biodiesel as Motor Fuel

The major disadvantages of biodiesel are higher viscosity, lower energy content, higher cloud point and pour point, higher nitrogen oxides (NO_x) emissions, lower engine speed and power, injector coking, engine compatibility, high price, and higher engine wear.

Table 4.39 shows the fuel ASTM Standards of biodiesel and petroleum diesel fuels. Important operating disadvantages of biodiesel in comparison with petrodiesel are cold start problems, the lower energy content, higher copper strip corro-

Table 4.39 ASTM Standards of biodiesel and petrodiesel fuels

Property	Test Method	ASTM D975 (Petroleum Diesel)	ASTM D6751 (Biodiesel, B100)
Flash Point	D 93	325 K min	403 K
Water and Sediment	D 2709	0.05 max %vol	0.05 max %vol
Kinematic Viscosity (at 313 K)	D 445	1.3–4.1 mm ² /s	1.9–6.0 mm ² /s
Sulfated Ash	D 874	–	0.02 max %wt
Ash	D 482	0.01 max %wt	–
Sulfur	D 5453	0.05 max %wt	–
Sulfur	D 2622/129	–	0.05 max %wt
Copper Strip Corrosion	D 130	No. 3 max	No 3 max
Cetane Number	D 613	40 min	47 min
Aromaticity	D 1319	35 max %vol	–
Carbon Residue	D 4530	–	0.05 max %mass
Carbon Residue	D 524	0.35 max %mass	–
Distillation Temp (90% Volume Recycle)	D 1160	555 K min–611 K max	–

sion, and fuel pumping difficulty due to higher viscosity. This increases fuel consumption when biodiesel is used in comparison with application of pure petrodiesel, in proportion to the share of the biodiesel content. Taking into account the higher production value of biodiesel as compared to petrodiesel, this increase in fuel consumption in addition raises the overall cost of application of biodiesel as an alternative to petrodiesel.

Biodiesel has a higher cloud point and a higher pour point compared to conventional diesel. Neat biodiesel and biodiesel blends increase nitrogen oxides (NO_x) emissions compared with petroleum-based diesel fuel used in an unmodified diesel engine (EPA, 2002). The peak torque is less for biodiesel than petroleum diesel but occurs at lower engine speed, and generally the torque curves are flatter. The biodiesels on the average decrease power by 5% compared to diesel at the rated load.

4.6.12 Engine Performance Tests

Biodiesel, commercial diesel fuel, and their blends were used as the fuel of a direct injection (DI) compression ignition engine. Criteria pollutant emissions from biodiesel blends are now becoming a relevant subject due to the increase in consumption of this renewable fuel worldwide. Biodiesel is the first and only alternative fuel to commercial diesel to have a complete evaluation of emission results. The exhaust gas emissions are reduced with an increase in biodiesel concentration of the fuel blend. The emission forming gases such as carbon dioxide and carbon monoxide from combustion of biodiesel hydrocarbons are generally less than those of diesel fuel. The lower percentage of biodiesel blends emits very low amount of carbon dioxide (CO_2) in comparison with diesel. The engine emits more carbon monoxide (CO) using diesel as compared to that of biodiesel blends under all loading conditions. With increasing biodiesel percentage, CO emission level decreases. Sulfur emissions are essentially eliminated with pure biodiesel. The torque values of commercial diesel fuel are greater than those of biodiesel. The brake power of biodiesel is nearly the same as with diesel fuel. The specific fuel consumption values of biodiesel are greater than those of commercial diesel fuel. The effective efficiency and effective pressure values of commercial diesel fuel are greater than those of biodiesel. Biodiesel methyl esters improve the lubrication properties of the diesel fuel blend. Biodiesel reduced long-term engine wear in diesel engines. Even biodiesel levels below 1% can provide up to a 30% increase in lubricity.

Biodiesel and petroleum-based diesel have similar fuel properties, *e.g.*, viscosity, heating value, boiling temperature, cetane number, *etc.* For this reason, biodiesel may be used in standard diesel engines. The only modifications required are a two-to-three degree retardation of injection timing and replacement of all natural rubber seals with synthetic ones, due to the solvent characteristics of biodiesel. The kinematic viscosity values of biodiesels are between $3.6 \text{ mm}^2/\text{s}$ and $4.6 \text{ mm}^2/\text{s}$.

From an operational point of view, biodiesel has about 90% of the energy content of petroleum diesel, measured on a volumetric basis. Due to this fact, on average basis the use of biodiesel reduces the fuel economy and power by about 10% in comparison with petroleum diesel. The reason for this improvement stems mainly from the oxygen content of biodiesel, the ensuing better combustion process, and the improved lubricity, which partly compensate the impact of the lower energy content. Biodiesel is an oxygenated compound. Oxygenates are just preused hydrocarbons having a structure that provides a reasonable antiknock value. Also, as they contain oxygen, fuel combustion is more efficient, reducing hydrocarbons in exhaust gases. The only disadvantage is that oxygenated fuel has less energy content. For the same efficiency and power output, more fuel has to be burned. On the other hand, biodiesel blends are safer than pure petroleum diesel, because biodiesel has a higher flash point. Most operational disadvantages of pure biodiesel, *e.g.*, replacement of natural rubber seals, cold start problems, *etc.*, do not arise when using blended kinds of biodiesel.

Fuel characterization data show some similarities and differences between biodiesel and diesel fuels (Shay, 1993):

- The specific weight is higher for biodiesel, heat of combustion is lower, and viscosities are 1.3–1.6 times that of No. 2 diesel fuel.
- Pour points for biodiesel fuels vary from 1–25°C higher for biodiesel fuels, depending on the feedstock.
- The sulfur content for biodiesel fuel is 20–50% that of No. 2 diesel fuel.
- The methyl esters all have higher levels of injector coking than No. 2 diesel fuel.

In cities across the globe, the personal automobile is the single greatest polluter, as emissions from millions of vehicles on the road add up to a planet-wide problem. The biodiesel impacts on exhaust emissions vary depending on the type of biodiesel and on the type of conventional diesel. Blends of up to 20% biodiesel mixed with petroleum diesel fuels can be used in nearly all diesel equipment and are compatible with most storage and distribution equipment. Using biodiesel in a conventional diesel engine substantially reduces emissions of unburned hydrocarbons, carbon monoxide, sulfates, polycyclic aromatic hydrocarbons, nitrated polycyclic aromatic hydrocarbons, and particulate matter. These reductions increase as the amount of biodiesel blended into diesel fuel increases. In general, biodiesel increases NO_x emissions when used as fuel in a diesel engine. The fact that NO_x emissions increase with increasing biodiesel concentration may be a detriment in areas that are out of attainment for ozone.

Biodiesel provides significant lubricity improvement over petroleum diesel fuel. Lubricity results of biodiesel and petroleum diesel using industry test methods indicate that there is a marked improvement in lubricity when biodiesel is added to conventional diesel fuel. Even biodiesel levels below 1% can provide up to a 30% increase in lubricity.

In general, biodiesel will soften and degrade certain types of elastomers and natural rubber compounds over time. Using high percent blends can impact fuel system components (primarily fuel hoses and fuel pump seals), that contain elas-

omer compounds incompatible with biodiesel. Manufacturers recommend that natural or butyl rubbers not be allowed to come in contact with pure biodiesel. Biodiesel will lead to degradation of these materials over time, although the effect is lessened with biodiesel blends.

Biodiesel has demonstrated a number of promising characteristics, including reduction of exhaust emissions. The combustion of biodiesel fuel in CIEs in general results in lower smoke, particulate matter, carbon monoxide, and hydrocarbon emissions compared to standard diesel fuel combustion, while the engine efficiency is either unaffected or improved. The increased in-cylinder pressure and temperature lead to increased NO_x emissions, while the more advanced combustion assists in the reduction of smoke compared to pure diesel combustion. The advanced rapeseed methyl ester combustion resulted in the reduction of smoke, HC, and CO, while both NO_x emissions and fuel consumption were increased.

The commercial biodiesel fuel significantly reduces PM exhaust emissions (75–83%) compared to the petrodiesel base fuel. However, NO_x exhaust emissions increases slightly with commercial biodiesel compared to the base fuel. The chain length of the compounds has little effect on NO_x and PM exhaust emissions, while the influence is greater on HC and CO, the latter being reduced with decreasing chain length. Non-saturation in the fatty compounds causes an increase in NO_x exhaust emissions.

In a previous study (Canakci, 2007), the combustion characteristics and emissions of two different petroleum diesel fuels (No. 1 and No. 2) and biodiesel from soybean oil were compared. Then experimental results compared with No. 2 diesel fuel showed that biodiesel provided significant reductions in PM, CO, and unburned HC; the NO_x increased by 11.2%. Biodiesel had a 13.8% increase in brake-specific fuel consumption due to its lower heating value. However, using No. 1 diesel fuel gave better emission results, NO_x , and brake-specific fuel consumption reduced by 16.1% and 1.2%, respectively.

PM-10 emissions and power of a diesel engine fueled with crude and refined biodiesel from salmon oil has been investigated. The results indicate a maximum power loss of about 3.5% and also near 50% of PM-10 reduction with respect to diesel when a 100% of refined biodiesel is used. Previous research has shown that biodiesel-fueled engines produce less carbon monoxide (CO), unburned hydrocarbon (HC), and particulate emissions compared to mineral diesel fuel, but higher NO_x emissions (Demirbas, 2008). The addition of tobacco seed oil methyl ester to the diesel fuel reduced CO and SO_2 emissions while causing slightly higher NO_x emissions. Meanwhile, it was found that the power and the efficiency increased slightly with the addition of tobacco seed oil methyl ester. Biodiesel fueled engines produce less carbon monoxide, unburned hydrocarbons, and particulate emissions compared to diesel fuel.

The combustion of biodiesel alone provides over a 90% reduction in total unburned hydrocarbons and a 75–90% reduction in polycyclic aromatic hydrocarbons. Biodiesel further provides significant reductions in particulates than petroleum diesel fuel. This reduction is mainly caused by reduced soot formation and

enhanced soot oxidation. The oxygen content and the absence of aromatic content in biodiesel have been pointed out as being the main reasons for this.

The use of biodiesel to reduce N_2O is attractive for several reasons. Biodiesel contains little nitrogen, as compared with petrodiesel, which is also used as a re-burning fuel. The N_2O reduction is strongly dependent upon initial N_2O concentrations and only slightly dependent upon temperature, where increased temperature increases N_2O reduction. This results in lower N_2O production from fuel nitrogen species for biodiesel. In addition, biodiesel contains trace amounts of sulfur, so SO_2 emissions are reduced in direct proportion to the petrodiesel replacement.

Different scenarios for the use of agricultural residues as fuel for heat or power generation have been analyzed. Reductions in net CO_2 emissions are estimated at 77–104 g/MJ of diesel displaced by biodiesel. The predicted reductions in CO_2 emissions are much greater than values reported in recent studies on biodiesel derived from other vegetable oils, due both to the large amount of potential fuel in the residual biomass and to the low-energy inputs in traditional coconut farming techniques. Unburned hydrocarbon emissions from biodiesel fuel combustion decrease compared to regular petroleum diesel. Figure 4.26 shows a plot for decreasing of unburned hydrocarbon *versus* biodiesel in the mixture of diesel and biodiesel (Bala, 2005).

Biodiesel, produced from different vegetable oils, seems very interesting for several reasons: It can replace diesel oil in boilers and internal combustion engines without major adjustments, only a small decrease in performances is reported, almost zero emissions of sulfates, a small net contribution of CO_2 when the whole life-cycle is considered, the emission of pollutants is comparable with that of diesel oil. For these reasons, several campaigns have been planned in many countries to introduce and promote the use of biodiesel.

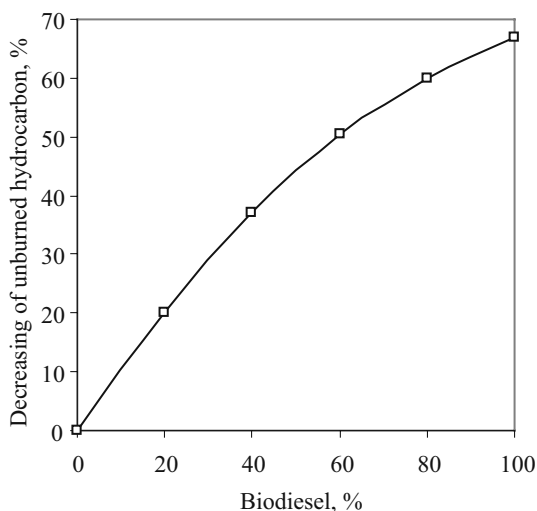


Fig. 4.26 Plot for decreasing of unburned hydrocarbon (%) *versus* biodiesel (%) in the mixture of diesel and biodiesel

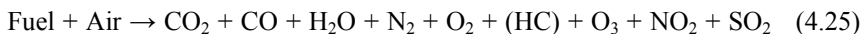
The use of blends of biodiesel and diesel oil are preferred in engines, in order to avoid some problems related to the decrease of power and torque, and to the increase of NO_x emissions with increasing content of pure biodiesel in the blend.

One of the most common blends of biodiesel contains 20 volume percent biodiesel and 80 volume percent conventional diesel (B20). For soybean-based biodiesel at this concentration, the estimated emission impacts for percent change in emissions of NO_x , PM, HC, and CO were +20%, -10.1%, -21.1%, and -11.0%, respectively (EPA, 2002). The use of blends of biodiesel and diesel oil are preferred in engines in order to avoid some problems related to the decrease of power and torque, and to the increase of NO_x emissions (a contributing factor in the localized formation of smog and ozone) that occurs with an increase in the content of pure biodiesel in a blend. Emissions of all pollutants except NO_x appear to decrease when biodiesel is used.

The lower percentage of biodiesel blends emits very low amount of CO_2 in comparison with diesel. B10 emits very low level of CO_2 emissions. Using higher concentration biodiesel blends as the fuel, CO_2 emission is found to increase. But, its emission level is lower than that of the diesel mode. B100 emits more amount of CO_2 , as compared to that of diesel operation. A larger amount of CO_2 in exhaust emission is an indication of the complete combustion of fuel. This supports the higher value of the exhaust gas temperature.

Emissions of regulated air pollutants, including CO, HC, NO_x , particulate matter (PM), and polycyclic aromatic hydrocarbons (PAHs) have been measured and results show that B20 use can reduce both PAH emission and its corresponding carcinogenic potency.

The typical engine combustion reaction is:



Carbon dioxide (CO_2) is a colorless, odorless, non-poisonous gas that results from fossil fuel combustion and is a normal constituent of ambient air. CO_2 does not directly impair human health, but it is a “greenhouse gas” that traps the Earth’s heat and contributes to the potential for global warming.

Carbon monoxide (CO) is a colorless, odorless, toxic gas produced by the incomplete combustion of carbon-containing substances. One of the major air pollutants, it is emitted in large quantities by exhaust from petroleum fuel-powered vehicles. CO is emitted directly from vehicle tailpipes. Incomplete combustion is most likely to occur at low air-to-fuel ratios in the engine. These conditions are common during vehicle starting when air supply is restricted, when cars are not tuned properly, and at altitude, where “thin” air effectively reduces the amount of oxygen available for combustion. Two-thirds of the carbon monoxide emissions come from transportation sources, with the largest contribution coming from highway motor vehicles. In urban areas, the motor vehicle contribution to carbon monoxide pollution can exceed 90%.

Under the high pressure and temperature conditions in an engine, nitrogen and oxygen atoms in the air react to form various nitrogen oxides, collectively known as NO_x . Nitrogen oxides, like hydrocarbons, are precursors to the formation of

ozone. They also contribute to the formation of acid rain. Nitric oxide (NO) is precursor of ozone, NO₂, and nitrate; usually emitted from combustion processes. Converted to nitrogen dioxide (NO₂) in the atmosphere, it then becomes involved in the photochemical process and/or particulate formation. Nitrogen oxides (NO_x) are gases formed in great part from atmospheric nitrogen and oxygen when combustion takes place under conditions of high temperature and high pressure; they are considered a major air pollutant and precursor of ozone.

Hydrocarbon (HC) emissions result when fuel molecules in an engine burn only partially. Some of the hydrocarbon compounds are major air pollutants; they may be active participants in the photochemical process or affect health. HCs react in the presence of nitrogen oxides and sunlight to form ground-level ozone, a major component of smog. Ozone irritates the eyes, damages the lungs, and aggravates respiratory problems. It is our most widespread and intractable urban air pollution problem. A number of exhaust hydrocarbons are also toxic, with the potential to cause cancer. Hydrocarbon pollutants also escape into the air through fuel evaporation; evaporative losses can account for a majority of the total hydrocarbon pollution from current model cars on hot days when ozone levels are highest.

Sulfur oxides (SO_x) are pungent, colorless gases formed primarily by the combustion of sulfur-containing fossil fuels, especially coal and oil. Considered major air pollutants, SO_x may impact human health and damage vegetation.

Ozone (O₃) is a pungent, colorless, toxic gas. Close to the Earth's surface it is produced photochemically from hydrocarbons, oxides of nitrogen, and sunlight, and is a major component of smog. At very high altitudes, it protects the Earth from harmful ultraviolet radiation.

Particulate matter (PM) is tiny solid or liquid particles of soot, dust, smoke, fumes, and aerosols. The size of the particles (10 microns or smaller) allows them to easily enter the air sacs in the lungs where they may be deposited, resulting in adverse health effects. PM also causes visibility reduction and is a criteria air pollutant.

Smog is a term used to describe many air pollution problems. Smog is a contraction of smoke and fog. Soot is very fine carbon particles that appear black when visible.

Combustion is a basic chemical process that releases energy from a fuel and air mixture. For combustion to occur, fuel, oxygen, and heat must be present together. The combustion is the chemical reaction of a particular substance with oxygen. Combustion represents a chemical reaction, during which from certain matter other simple matter are produced, this is a combination of inflammable matter with oxygen of the air accompanied by heat release. The quantity of heat evolved when one mole of a hydrocarbon is burned to carbon dioxide, and water is called the heat of combustion. Combustion to carbon dioxide and water is characteristic of organic compounds; under special conditions it is used to determine their carbon and hydrogen content. During combustion the combustible part of fuel is subdivided into volatile part and solid residue. During heating it evaporates together with a part of carbon in the form of hydrocarbon combustible gases and carbon monoxide release

by thermal degradation of the fuel. Carbon monoxide is mainly formed the following reactions: (a) from reduction of CO_2 with unreacted C,



and (b) from degradation of carbonyl fragments ($-\text{CO}$) in the fuel molecules at 600–750 K temperature.

The combustion process is started by heating the fuel above its ignition temperature in the presence of oxygen or air. Under the influence of heat, the chemical bonds of the fuel are cleaved. If complete combustion occurs, the combustible elements (C, H, and S) react with the oxygen content of the air to form CO_2 , H_2O , and mainly SO_2 .

If not enough oxygen is present or the fuel and air mixture is insufficient, then the burning gases are partially cooled below the ignition temperature, and the combustion process stays incomplete. The flue gases then still contain combustible components, mainly carbon monoxide (CO), unburned carbon (C), and various hydrocarbons (C_xH_y).

The standard measure of the energy content of a fuel is its heating value (HV), sometimes called the calorific value or heat of combustion. In fact, there are multiple values for HV, depending on whether it measures the enthalpy of combustion (ΔH) or the internal energy of combustion (ΔU), and whether for a fuel containing hydrogen product water is accounted for in the vapor phase or the condensed (liquid) phase. With water in the vapor phase, the lower heating value (LHV) at constant pressure measures the enthalpy change due to combustion. The heating value is obtained by the complete combustion of a unit quantity of solid fuel in an oxygen-bomb calorimeter under carefully defined conditions. The gross heat of combustion or higher heating value (GHC or HHV) is obtained by oxygen-bomb calorimeter method as the latent heat of moisture in the combustion products is recovered.

The methyl ester of vegetable oil has been evaluated as a fuel in CIEs by researchers (Kusdiana and Saka, 2001), who concluded that the performance of the esters of vegetable oil does not differ greatly from diesel fuel. The brake power of biodiesel was nearly the same as with diesel fuel, while the specific fuel consumption was higher than that of No. 2 diesel. Based on crankcase oil analysis, engine wear rates were low but some oil dilution did occur. Carbon deposits inside the engine were normal with the exception of intake valve deposits. The results showed that the transesterification treatment decreased the injector coking to a level significantly lower than that observed with No. 2 diesel fuel (Demirbas, 2007). Although most researchers agree that vegetable oil ester fuels are suitable for use in CIEs, a few contrary results have also been obtained. The results of these studies point out that most vegetable oil esters are suitable as diesel substitutes but that more long-term studies are necessary for commercial utilization to become practical.

Blends of up to 20% biodiesel mixed with petroleum diesel fuels can be used in nearly all diesel equipment and are compatible with most storage and distribution equipment. Higher blends, even B100, can be used in many engines built with

little or no modification. Transportation and storage, however, require special management. Material compatibility and warrantee issues have not been resolved with higher blends.

Because alcohols have limited solubility in diesel, stable emulsion must be formed that will allow it to be injected before separation occurs. A hydro-shear emulsification unit can be used to produce emulsions of diesel-alcohol. However, the emulsion can only remain stable for 45 seconds. In addition, 12% alcohol (energy basis) is the maximum percentage. This kind of method has several problems, which are as follows: (a) specific fuel consumption at low speed increases, (b) high cost, and (c) instability. Therefore, other methods have been developed.

To reduce the high viscosity of vegetable oils, microemulsions with immiscible liquids such as methanol and ethanol and ionic or non-ionic amphiphiles have been studied (Ma and Hanna, 1999). The short engine performances of both ionic and non-ionic microemulsions of ethanol in soybean oil were nearly as good as that of No. 2 diesel fuel (Goering *et al.*, 1982).

All microemulsions with butanol, hexanol, and octanol met the maximum viscosity requirement for No. 2 diesel fuel. 2-octanol was found an effective amphiphile in the micellar solubilization of methanol in triolein and soybean oil (Ma and Hanna, 1999).

A fumigation system injects a gaseous or liquid fuel into the intake air stream of a compression ignited engine. This fuel burns and becomes a part-contributor to the power producing fuel. While alcohol and gasoline may be used, gaseous fumigation seems to exhibit the best overall power yields, performance, and emissions benefits. Rudolf Diesel's 1901 patent mentions the diesel fumigation process. It was not until the 1940s that there were any commercial fumigation applications. Fumigation with propane has been studied as a means to reduce injector coking.

Fumigation is a process of introducing alcohol into the diesel engine (up to 50%) by means of a carburetor in the inlet manifold. At the same time, the diesel pump operates at a reduced flow. In this process, No. 2 diesel fuel is used for generating a pilot flame and alcohol is used as a fumigated fuel.

Alcohol is used as a fumigated fuel. At low loads, the quantity of alcohol must be reduced to prevent misfire. On the other hand, at high loads, the quantity of alcohol must also be reduced to prevent preignition.

In dual injection systems, a small amount of diesel is injected as a pilot fuel for the ignition source. A large amount of alcohol is injected as the main fuel. It must be noted that the pilot fuel must be injected prior to injection of the alcohol. Some ideal results can be achieved when this method is used. Thermal efficiency is better and, at the same time, NO_x emission is lower. Moreover, CO emissions and HC emissions are the same. However, the system requires two fuel pumps, thus, leading to a high cost. Moreover, alcohol needs additives for lubricity.

A visual inspection of the injector types would indicate no difference between the biodiesels when tested on No. 2 diesel fuel. The overall injector coking is considerably low. Linear regression is used to compare injector coking, viscosity, percent of biodiesel, total glycerol, and heat of combustion data with the others.

Alcohol can ignite with hot surfaces. For this reason, glow-plugs can be utilized as a source of ignition for alcohol. In this system, specific fuel consumption depends on glow-plug positions and temperatures. It must be noted that the temperature of glow-plugs must vary with load. However, the glow-plug becomes inefficient at a high load. In addition, the specific fuel consumption is higher than that of diesel.

The peak torque is less for biodiesel fuels than for No. 2 diesel fuel but occurs at lower engine speed, and generally the torque curves are flatter. Testing includes the power and torque of the methyl esters and diesel fuel, and ethyl esters *versus* diesel fuel. Biodiesels on the average decrease power by 5% compared to that of diesel at rated load.

When a spark plug is used, a diesel engine can be converted to an Otto cycle engine. In this case, the compression ratio should be reduced from 16:1 to 10.5:1. There are two types of this kind of conversion. They are as follows: (a) The original fuel injection system is maintained. Alcohol needs additive for lubricity. Besides, both distributor and sparkplug need to be installed, thus leading to a high cost of conversion. It is critical to adjust an ideal injection and spark-time for this kind of conversion. (b) Original fuel injection is eliminated. But, a carburetor, a spark-plug, and a distributor need to be installed, which increases the cost of conversion. In this conversion, spark timing is critical.

The effects of oxidative degradation caused by contact with ambient air (autoxidation) during long-term storage present a legitimate concern in terms of maintaining the fuel quality of biodiesel. Oxidative degradation reactions of biodiesel fuels have been conducted in the laboratory under varying time and temperature conditions (Dunn, 2002). Results showed that the reaction time significantly affects kinematic viscosity (ν). With respect to increasing reaction temperature, ν , acid value (AV), peroxide value (PV), and specific gravity (SG) increased significantly, whereas cold flow properties were minimally affected for temperatures up to 423 K. Antioxidants tert-butylhydroquinone (TBHQ) and α -tocopherol showed beneficial effects on retarding the oxidative degradation of methyl soyate (biodiesel) under the conditions of this study. Results indicated that ν and AV have the best potential as parameters for timely and easy monitoring of biodiesel fuel quality during storage. TBHQ is the most effective antioxidant for highly unsaturated vegetable oils and many animal fats.

4.6.12.1 Evaluation of Engine Performance Using Biodiesel

Through its combustion of fossil fuels the average vehicle emits greenhouse gases like carbon dioxide, methane, nitrous oxide, and chlorofluorocarbons that surround the Earth's atmosphere like a clear thermal blanket allowing the sun's warming rays in and trapping the heat close to Earth's surface. By reducing vehicular emission alternate fuels help combat both air pollution and global climate change. There is a growing concern that world may run out of petroleum based fuel re-

sources. All these issues make it imperative that search for alternative fuels is taken earnestly.

Biodiesels are monoalkyl esters containing approximately 10% oxygen by weight. The oxygen improves the efficiency of combustion, but it takes up space in the blend and therefore slightly increases the apparent fuel consumption rate observed while operating an engine with biodiesel. Current investigations reveal that the engine performance with diesel–biodiesel blends is comparable with diesel fuel operation. Technical aspects of biodiesel are approached, such as the physical and chemical characteristics of methyl esters related to its performance in CIEs. When testing an engine in a test bench, equivalent performance requires attaining the same engine speed and torque, regardless of the fuel used. A meaningful comparison of emissions and fuel consumption is only possible if tests are carried out under the same operation mode.

The high combustion temperature at high engine speed becomes the dominant factor, making both heated and unheated fuel to acquire the same temperature before fuel injection. Various methods of using vegetable oil (jatropha oil) and methanol such as blending, transesterification and dual fuel operation have been studied experimentally (He and Bao, 2003). Brake thermal efficiency was better in the dual fuel operation and with the methyl ester of jatropha oil as compared to the blend. It increased from 27.4% with neat jatropha oil to a maximum of 29% with the methyl ester and 28.7% in the dual fuel operation (He and Bao, 2003).

The performance of the esters of vegetable oil does not differ greatly from that of diesel fuel. The brake power is nearly the same as with diesel fuel, while the specific fuel consumption is higher than that of diesel fuel. Carbon deposits inside the engine were normal, with the exception of intake valve deposits. It was shown that biodiesel decreased the injector coking to a level significantly lower than that observed with No 2 diesel fuel.

Various engine performance parameters such as thermal efficiency, brake specific fuel consumption (BSFC), and brake specific energy consumption (BSEC), *etc.*, can be calculated from the acquired data. The torque, brake power and fuel consumption values associated with CIE fuels were determined under certain operating conditions. In an earlier study (Shay, 1993), the physical and chemical properties of ethyl ester produced from sunflower oil were similar to diesel fuel. After the test was conducted, it was observed that sunflower oil ethyl ester (ethylic biodiesel) gives similar results at short period performance tests. However, there was a huge difference between the specific fuel consumption values of fuels at the same speed values. In the studies, the measured difference in torque values for diesel fuel and the ethyl ester was calculated as 8% at 2400 min^{-1} , where the maximum engine moment was measured. The difference in torque values of these fuels was calculated as 18% at 3900 min^{-1} , where the maximum power was measured. The difference of effective powers was calculated as 10% and 17%, respectively, at same speed values. The differences of smoke values were calculated as 14% at speed level where the maximum moment was measured, and 22% at speed level where the maximum power was obtained. The ethylic biodiesel has lower noise level than that of the diesel fuel at all engine speed (Shay, 1993). Calcula-

tions of the fuel conversion efficiency, based on the lower heating value of the fuel, showed that all of the biodiesel fuels had the same efficiency. This indicates that regardless of the degree of saturation of the ester, there are no fundamental changes in the way the different esters burn in the engine.

Kaplan *et al.* (2006) compared sunflower oil biodiesel and diesel fuels at full and partial loads and at different engine speeds in a 2.5153 kW engine. The loss of torque and power ranged between 5% and 10%, and particularly at full load, the loss of power was closer to 5% at low speed and to 10% at high speed.

Petroleum diesel fuel and ethylic biodiesel fuel were tested in a naturally aspirated direct injected (DI) diesel engine in four steady operation modes, defined by their engine speed and brake mean effective pressure, the latter being proportional to the effective torque (Kaplan *et al.*, 2006). In earlier studies, the operation modes selected tried to simulate representative engine conditions, often taking as reference certification cycles, which in the case of heavy-duty engines cover the whole load range (concentrating mainly on 25%, 50%, 75%, and 100% of maximum torque) at various speeds and, in the case of vehicle engines, are concentrated around the low–medium load (Puhan *et al.*, 2005).

In an earlier study (Canakci *et al.*, 2006), the tests were performed with commercial diesel fuel and biodiesel. The experimental results of the commercial diesel fuel are listed in Table 4.40. Table 4.41 shows the experimental results of the biodiesel fuel (Ozkan *et al.*, 2005). Using Tables 4.40 and 4.41, the performance curves for the fuels are shown together for comparison purposes. The maximum brake power values of biodiesel and diesel were 4.390 kW and 5.208 kW obtained at 2750 and 2500 rpm, respectively. According to these values, the commercial diesel fuel has the greatest brake power. Compared to diesel fuel, a 25% power loss occurred with biodiesel. The maximum torque values are about 21.0 Nm at 1500 rpm for the diesel fuel and 19.7 Nm at 1500 rpm for the biodiesel. The torque values of commercial diesel fuel are greater than those of biodiesel. The specific fuel consumption values of biodiesel are greater than those of commercial diesel fuel. The effective efficiency and effective pressure values of commercial diesel fuel are greater than those of biodiesel (Canakci *et al.*, 2006).

Fuel consumption at full load condition and low speeds generally is high. Fuel consumption first decreases and then increases with increasing speed. The reason is that the produced power in low speeds is low and the main part of fuel is consumed to overcome the engine friction (Ozkan *et al.*, 2005).

The trend of the performance curves concerning power and torque are very much like those mentioned in valid concerned literature. The range of speed was selected between 1200 and 3600 rpm. Considering power and torque performance with fuel blends, one can say that the trend of these parameters *versus* speed is perfectly similar to diesel fuel. Engine test results with diesel fuel showed that the maximum torque was 64.2 Nm, which occurred at 2400 rpm. The maximum power was 18.12 kW at 3200 rpm (Najafi *et al.*, 2007).

Biodiesel methyl esters improve the lubrication properties of the diesel fuel blend. Fuel injectors and some types of fuel pumps rely on fuel for lubrication. Biodiesel reduced long-term engine wear in test diesel engines to less than half of

Table 4.40 Experimental results of commercial diesel fuel

Engine speed (Rpm)	Torque (Nm)	Power (kW)	SFC ^a (g/kWh)	Effective efficiency (%)	Effective pressure (bar)
1000	20.2	2.119	380.498	22.6	5.600
1250	20.8	2.716	395.718	22.7	5.744
1500	21.0	3.300	346.706	24.8	5.816
1750	19.9	3.641	324.722	26.5	5.500
2000	19.9	4.156	304.825	28.2	5.493
2250	19.8	4.651	282.468	30.4	5.464
2500	19.9	5.208	272.411	31.6	5.507
2750	16.9	4.877	290.880	29.6	4.688
3000	13.5	4.229	349.462	24.6	3.726

^aSFC: Specific fuel consumption.**Table 4.41** Experimental results of biodiesel fuel

Engine speed (Rpm)	Torque (Nm)	Power (kW)	SFC ^a (g/kWh)	Effective efficiency (%)	Effective pressure (bar)
1000	17.8	1.861	471.859	18.23	4.919
1250	17.2	2.246	433.236	19.85	4.749
1500	17.2	2.695	417.441	20.60	4.749
1750	17.7	3.234	359.089	23.95	4.885
2000	18.0	3.768	341.232	25.20	4.980
2250	18.4	4.331	307.841	27.94	5.089
2500	15.9	4.171	331.977	25.91	4.410
2750	15.3	4.390	341.664	25.17	4.220
3000	9.6	3.018	372.715	23.07	2.660

^aSFC: Specific fuel consumption

what was observed in engines running on current low sulfur diesel fuel. Lubricity properties of fuel are important for reducing friction wear in engine components, normally lubricated by the fuel rather than crankcase oil (Ma and Hanna, 1999; Demirbas, 2003a). Lubricity results of biodiesel and petroleum diesel using industry test methods indicate that there is a marked improvement in lubricity when biodiesel is added to conventional diesel fuel. Even biodiesel levels below 1% can provide up to a 30% increase in lubricity (Demirbas, 2008).

Using biodiesel in a conventional diesel engine substantially reduces emissions of unburned hydrocarbons, carbon monoxide, sulfates, polycyclic aromatic hydrocarbons, nitrated polycyclic aromatic hydrocarbons, and particulate matter. These reductions increase as the amount of biodiesel blended into diesel fuel increases. The best emission reductions are seen with B100 (100% biodiesel). The biodiesel sulfur content is another interesting advantage of the produced fuel, which is 18 ppm only. Comparing the 18 ppm sulfur content of the produced biodiesel with the 500 ppm sulfur content of the diesel fuel, the advantage of the biodiesel over

the diesel fuel in terms of the environmental benefits can be justified (Ozkan *et al.*, 2005).

Biodiesel fuels can be performance improving additives in compression ignition engines. Performance testing showed that while the power decreased and the brake specific fuel consumption increased for all of the biodiesel samples, compared with No. 2 diesel fuel, the amounts of the changes were in direct proportion to the lower energy content of the biodiesel.

Biodiesel is a biodegradable and renewable fuel. It contributes no net carbon dioxide or sulfur to the atmosphere and emits less gaseous pollutants than normal diesel. Carbon monoxide, aromatics, polycyclic aromatic hydrocarbons (PAHs), and partially burned or unburned hydrocarbon emissions are all reduced in vehicles operating on biodiesel.

4.7 Bio-oils from Biorenewables

The term bio-oil is used mainly to refer to liquid fuels from biorenewable feedstocks. Biomass is heated in the absence of oxygen, or partially combusted in a limited oxygen supply, to produce an oil-like liquid, a hydrocarbon rich gas mixture and a carbon rich solid residue. Pyrolysis dates back to at least ancient Egyptian times, when tar for caulking boats and certain embalming agents were made by pyrolysis. In the 1980s, researchers found that the pyrolysis liquid yield could be increased using fast pyrolysis where a biomass feedstock is heated at a rapid rate and the vapors produced are also condensed rapidly (Mohan *et al.*, 2006).

In wood derived pyrolysis oil, specific oxygenated compounds are present in relatively large amounts. A current comprehensive review focuses on the recent developments in the wood/biomass pyrolysis and reports the characteristics of the resulting bio-oils, which are the main products of fast wood pyrolysis (Mohan *et al.*, 2006). Sufficient hydrogen added to the synthesis gas to convert all of the biomass carbon into methanol carbon would more than double the methanol produced from the same biomass base.

Pyrolysis is the simplest and almost certainly the oldest method of processing one fuel in order to produce a better one. Pyrolysis can also be carried out in the presence of a small quantity of oxygen (“gasification”), water (“steam gasification”), or hydrogen (“hydrogenation”). One of the most useful products is methane, which is a suitable fuel for electricity generation using high-efficiency gas turbines. The main pyrolysis methods and their variants are listed in Table 4.42.

Biomass pyrolysis is attractive because solid biomass and wastes can be readily converted into liquid products. These liquids, such as crude bio-oil or slurry of charcoal of water or oil, have advantages in transport, storage, combustion, retrofitting, and flexibility in production and marketing.

The pyrolysis of biomass is a thermal treatment that results in the production of charcoal, liquid, and gaseous products. Among the liquid products, methanol is one of the most valuable products. The liquid fraction of the pyrolysis products

Table 4.42 Pyrolysis methods and their variants

Method	Residence time	Temperature, K	Heating rate	Products
Carbonation	days	675	very low	charcoal
Conventional	5–30 min	875	low	oil, gas, char
Fast	0.5–5 s	925	very high	bio-oil
Flash-liquid ^a	<1 s	<925	high	bio-oil
Flash-gas ^b	<1 s	<925	high	chemicals, gas
Hydropyrolysis ^c	<10 s	<775	high	bio-oil
Methano-pyrolysis ^d	<10 s	>975	high	chemicals
Ultra pyrolysis ^e	<0.5 s	1275	very high	chemicals, gas
Vacuum pyrolysis	2–30 s	675	medium	bio-oil

^aFlash-liquid: liquid obtained from flash pyrolysis accomplished in a time of <1 s.

^bFlash-gas: gaseous material obtained from flash pyrolysis within a time of <1 s.

^cHydropyrolysis: pyrolysis with water.

^dMethanopyrolysis: pyrolysis with methanol.

^eUltra pyrolysis: pyrolyses with very high degradation rate.

consists of two phases: an aqueous phase containing a wide variety of organo-oxygen compounds of low molecular weight and a non-aqueous phase containing insoluble organics of high molecular weight. This phase is called tar and is the product of greatest interest. The ratios of acetic acid, methanol, and acetone of the aqueous phase were higher than those of the non-aqueous phase. The point where the cost of producing energy from fossil fuels exceeds the cost of biomass fuels has been reached. With a few exceptions, energy from fossil fuels will cost more money than the same amount of energy supplied through biomass conversion.

Table 4.43 shows the fuel properties of diesel, biodiesel and biomass pyrolysis oil. The kinematic viscosity of pyrolysis oil varies from as low as 11 cSt to as high as 115 mm²/s (measured at 313 K), depending on nature of the feedstock, temperature of pyrolysis process, thermal degradation degree and catalytic cracking, the water content of the pyrolysis oil, the amount of light ends that have collected, and the pyrolysis process used. The pyrolysis oils have a water content of typically 15–30 wt% of the oil mass, which cannot be removed by conventional methods like distillation. Phase separation may partially occur above certain water contents. The water content of pyrolysis oils contributes to their low energy density, lowers the flame temperature of the oils, leads to ignition difficulties, and, when preheating the oil, can lead to premature evaporation of the oil and resultant injection difficulties. The higher heating value (HHV) of pyrolysis oils is below 26 MJ/kg (compared to 42–45 MJ/kg for compared to values of 42–45 MJ/kg for conventional petroleum fuel oils). In contrast to petroleum oils, which are non-polar and in which water is insoluble, biomass oils are highly polar and can readily absorb over 35% water (Demirbas, 2007).

The pyrolysis oil (bio-oil) from wood is typically a liquid, almost black through dark red to brown. The density of the liquid is about 1200 kg/m³, which is higher than that of fuel oil and significantly higher than that of the original biomass. Bio-oils have a water content of typically 14–33 wt.%, which cannot be removed by

Table 4.43 Fuel properties of diesel, biodiesel and biomass pyrolysis oil

Property	Test method	ASTM D975 (Diesel)	ASTM D6751 (Biodiesel, B100)	Pyrolysis Oil (Bio-oil)
Flash Point	D 93	325 K min	403 K	—
Water and sediment	D 2709	0.05 max %vol	0.05 max %vol	0.01–0.04
Kinematic viscosity (at 313 K)	D 445	1.3–4.1 mm ² /s	1.9–6.0 mm ² /s	25–1000
Sulfated ash	D 874	—	0.02 max %wt	—
Ash	D 482	0.01 max %wt	—	0.05–0.01 %wt
Sulfur	D 5453	0.05 max %wt	—	—
Sulfur	D 2622/129	—	0.05 max %wt	0.001–0.02%wt
Copper strip Corrosion	D 130	No 3 max	No 3 max	—
Cetane number	D 613	40 min	47 min	—
Aromaticity	D 1319	—	35 max %vol	—
Carbon residue	D 4530	—	0.05 max %mass	0.001–0.02%wt
Carbon residue	D 524	0.35 max %mass	—	—
Distillation temperature	D 1160	555 K min –611 K max	—	—

conventional methods like distillation. Phase separation may occur above certain water contents. The higher heating value (HHV) is below 27 MJ/kg (compared to 43–46 MJ/kg for conventional fuel oils).

The bio-oil formed at 725 K contained high concentrations of compounds such as acetic acid, 1-hydroxy-2-butanone, 1-hydroxy-2-propanone, methanol, 2,6-dimethoxyphenol, 4-methyl-2,6-dimethoxyphenol, 2-cyclopenten-1-one, *etc.* A significant characteristic of bio-oils was the high percentage of alkylated compounds especially methyl derivatives. As the temperature increased, some of these compounds were transformed *via* hydrolysis (Kuhlmann *et al.*, 1994). The formation of unsaturated compounds from biomass materials generally involves a variety of reaction pathways such as dehydration, cyclization, Diels–Alder cycloaddition reactions, and ring rearrangement. For example, 2,5-hexanedione can undergo cyclization under hydrothermal conditions to produce 3-methyl-2-cyclopenten-1-one with very high selectivity of up to 81% (An *et al.*, 1997).

The mechanism of pyrolysis reactions of biomass was extensively discussed in an earlier study (Demirbas, 2000). Water is formed by dehydration. In the pyrolysis reactions, methanol arises from the breakdown of methyl esters and/or ethers from decomposition of pectin-like plant materials. Methanol also arises from methoxyl groups of uronic acid (Demirbas and Güllü, 1998). Acetic acid is formed in the thermal decomposition of all three main components of wood. When the yield of acetic acid originating from the cellulose, hemicelluloses, and lignin is taken into account, the total is considerably less than the yield from the wood itself. Acetic acid comes from the elimination of acetyl groups originally linked to the xylose unit.

Furfural is formed by dehydration of the xylose unit. Quantitatively, 1-hydroxy-2-propanone and 1-hydroxy-2-butanone present high concentrations in the liquid products. These two alcohols are partly esterified by acetic acid. In conven-

tional slow pyrolysis, these two products are not found in so great a quantity because of their low stability (Beaumont, 1985).

If wood is completely pyrolyzed, the resulting products are about what would be expected when pyrolyzing the three major components separately. The hemicelluloses would break down first at temperatures of 470 to 530 K. Cellulose follows in the temperature range 510–620 K, with lignin being the last component to pyrolyze at temperatures of 550–770 K. A wide spectrum of organic substances was contained in the pyrolytic liquid fractions given in the literature (Beaumont, 1985). Degradation of xylan yields eight main products: water, methanol, formic, acetic and propionic acids, 1-hydroxy-2-propanone, 1-hydroxy-2-butanone, and 2-furfuraldehyde. The methoxy phenol concentration decreased with increasing temperature, while phenols and alkylated phenols increased. The formation of both methoxy phenol and acetic acid was possibly as a result of the Diels–Alder cycloaddition of a conjugated diene and unsaturated furanone or butyrolactone.

Timell (1967) described the chemical structure of the xylan as the 4-methyl-3-acetylglucuronoxylan. It has been reported that the first runs in the pyrolysis of the pyroligneous acid consist of about 50% methanol, 18% acetone, 7% esters, 6% aldehydes, 0.5% ethyl alcohol, 18.5% water, and small amounts of furfural (Demirbas, 2000). Pyroligneous acids disappear in high-temperature pyrolysis.

The composition of the water soluble products was not ascertained but it has been reported to be composed of hydrolysis and oxidation products of glucose such as acetic acid, acetone, simple alcohols, aldehydes, sugars, *etc.* (Sasaki *et al.*, 1998). Pyroligneous acids disappear in high-temperature pyrolysis. Levoglucosan is also sensitive to heat and decomposes to acetic acid, acetone, phenols, and water. Metha-

Table 4.44 Chemical and physical properties of biomass bio-oils and fuel oils

	Pine	Oak	Poplar	Hardwood	No. 2 oil	No. 6 oil
Elemental (wt% dry)						
C	56.3	55.6	59.3	58.8	87.3	87.7
H	6.5	5.0	6.6	9.7	12.0	10.3
O	36.9	39.2	33.8	31.2	0.0	1.2
N	0.3	0.1	0.2	0.2	<0.01	0.5
S	—	0.0	0.00	0.04	0.1	0.8
Proximate (wt%)						
ash	0.05	0.05	<0.001	0.07	<0.001	0.07
water	18.5	16.1	27.2	18.1	0.0	2.3
volatiles	66.0	69.8	67.4	—	99.8	94.1
fixed C	15.5	14.1	5.4	—	0.1	3.6
Viscosity (mm ² /s) at 313 K	44	115	11	58	2.6	—
Density (kg/m ³) at 313 K	1210	1230	—	1170	860	950
Pyrolysis yield (wt%)						
dry oil	58.9	55.3	41.0	—	—	—
water	13.4	10.4	14.6	—	—	—
char	19.6	12.2	16.4	—	—	—
gases	13.9	12.4	21.7	—	—	—

Source: Demirbas, 2007

nol arises from the methoxyl groups of aronic acid (Demirbas, 2000). Table 4.44 shows the chemical and physical properties of biomass bio-oils and fuel oils.

Table 4.45 shows the gas chromatographic analysis of bio-oil from beech wood pyrolysis (wt% dry basis). The bio-oil formed at 725 K contained high concentra-

Table 4.45 Gas chromatographic analysis of bio-oil from beech wood pyrolysis (wt% dry basis)

Compound	Reaction temperature (K)					
	625	675	725	775	825	875
Acetic acid	16.8	16.5	15.9	12.6	8.42	5.30
Methyl acetate	0.47	0.35	0.21	0.16	0.14	0.11
1-hydroxy-2-propanone	6.32	6.84	7.26	7.66	8.21	8.46
Methanol	4.16	4.63	5.08	5.34	5.63	5.82
1-hydroxy-2-butanone	3.40	3.62	3.82	3.88	3.96	4.11
1-hydroxy-2-propane acetate	1.06	0.97	0.88	0.83	0.78	0.75
Levoglucosan	2.59	2.10	1.62	1.30	1.09	0.38
1-hydroxy-2-butanone acetate	0.97	0.78	0.62	0.54	0.48	0.45
Formic acid	1.18	1.04	0.84	0.72	0.60	0.48
Guaiacol	0.74	0.78	0.82	0.86	0.89	0.93
Crotonic acid	0.96	0.74	0.62	0.41	0.30	0.18
Butyrolactone	0.74	0.68	0.66	0.67	0.62	0.63
Propionic acid	0.96	0.81	0.60	0.49	0.41	0.34
Acetone	0.62	0.78	0.93	1.08	1.22	1.28
2,3-butanedione	0.46	0.50	0.56	0.56	0.58	0.61
2,3-pentanedione	0.34	0.42	0.50	0.53	0.59	0.64
Valeric acid	0.72	0.62	0.55	0.46	0.38	0.30
Isovaleric acid	0.68	0.59	0.51	0.42	0.35	0.26
Furfural	2.52	2.26	2.09	1.84	1.72	1.58
5-methyl-furfural	0.65	0.51	0.42	0.44	0.40	0.36
Butyric acid	0.56	0.50	0.46	0.39	0.31	0.23
Isobutyric acid	0.49	0.44	0.38	0.30	0.25	0.18
Valerolactone	0.51	0.45	0.38	0.32	0.34	0.35
Propanone	0.41	0.35	0.28	0.25	0.26	0.21
2-butanone	0.18	0.17	0.32	0.38	0.45	0.43
Crotonolactone	0.12	0.19	0.29	0.36	0.40	0.44
Acrylic acid	0.44	0.39	0.33	0.25	0.19	0.15
2-Cyclopenten-1-one	1.48	1.65	1.86	1.96	2.05	2.13
2-Methyl-2-cyclopenten-1-one	0.40	0.31	0.24	0.17	0.13	0.14
2-methyl-cyclopentenone	0.20	0.18	0.17	0.22	0.25	0.29
Cyclopentenone	0.10	0.14	0.16	0.23	0.27	0.31
Methyl-2-furancarboxaldehyde	0.73	0.65	0.58	0.50	0.44	0.38
Phenol	0.24	0.30	0.36	0.43	0.54	0.66
2,6-dimethoxyphenol	2.28	2.09	1.98	1.88	1.81	1.76
Dimethyl phenol	0.08	0.13	0.18	0.42	0.64	0.90
Methyl phenol	0.32	0.38	0.44	0.50	0.66	0.87
4-methyl-2,6-dimethoxyphenol	2.24	2.05	1.84	1.74	1.69	1.58

Source: Demirbas, 2007

tions of compounds such as acetic acid, 1-hydroxy-2-butanone, 1-hydroxy-2-propanone, methanol, 2,6-dimethoxyphenol, 4-methyl-2,6-dimethoxyphenol, 2-cyclopenten-1-one, *etc.* A significant characteristic of the bio-oils was the high percentage of alkylated compounds, especially methyl derivatives.

The influence of temperature on the compounds existing in liquid products obtained from biomass samples *via* pyrolysis were examined in relation to the yield and composition of the product bio-oils. The product liquids were analyzed by a gas chromatography mass spectrometry combined system. The bio-oils were composed of a range of cyclopentanone, methoxyphenol, acetic acid, methanol, acetone, furfural, phenol, formic acid, levoglucosan, guaicol, and their alkylated phenol derivatives. Biomass structural components, such as cellulose, hemicelluloses, and were converted into liquids and gas products, as well as a solid residue of charcoal by thermal depolymerization and decomposition. The structural components of the biomass samples mainly affect pyrolytic degradation products. A reaction mechanism is proposed that describes a possible reaction route for the formation of the characteristic compounds found in the oils. The supercritical water extraction and liquefaction partial reactions also occur during the pyrolysis. Acetic acid is formed in the thermal decomposition of all three main components of biomass. In the pyrolysis reactions of biomass, water is formed by dehydration, acetic acid comes from the elimination of acetyl groups originally linked to the xylose unit, furfural is formed by dehydration of the xylose unit, formic acid proceeds from carboxylic groups of uronic acid, and methanol arises from methoxyl groups of uronic acid (Demirbas, 2007).

Figure 4.27 shows the plot for the yield of bio-oils from liquefaction of corn stover at subcritical and supercritical temperatures. The yields of bio-oils increase with increasing temperature. The yield of bio-oils sharply increases between 650 K and 680 K and then it reaches a plateau. This temperature range (650–680 K) is in

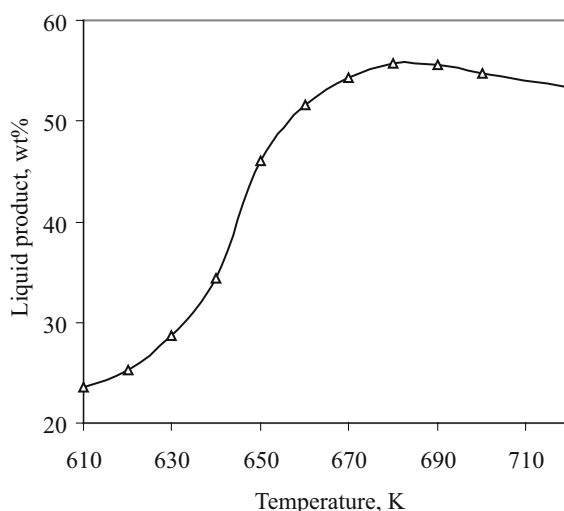


Fig. 4.27 Plot for the yield of liquid products from liquefaction of corn stover at subcritical and supercritical temperatures. Liquefaction time: 70 min. Water-to-solid ratio: 5:1

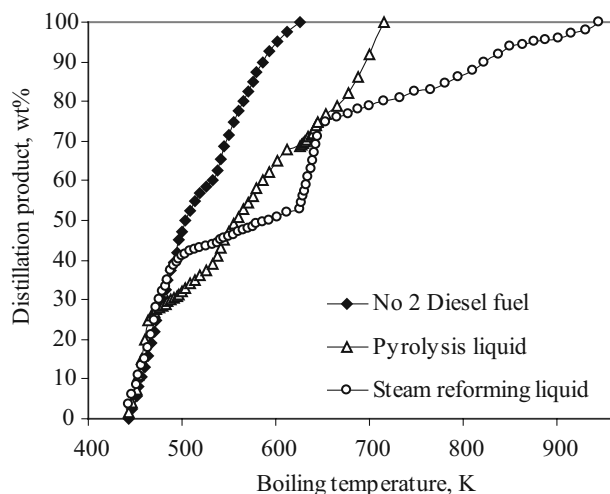


Fig. 4.28 Comparison of distillation curves of average distillation products obtained from pyrolysis and steam reforming of tallow to that of No. 2 diesel fuel

the supercritical zone. At temperatures higher than 690 K the yield of bio-oils are slightly lower. The maximum yield of bio-oil is obtained at reaction temperature 680 K. The highest bio-oil yield of 55.7% is obtained at reaction temperature 680 K, and the yield is 53.3% at 720 K.

Figure 4.28 shows a comparison of distillation curves of average distillation products obtained from pyrolysis and steam reforming of tallow to that of No 2 diesel fuel.

4.8 Other Alternate Liquid Fuels

4.8.1 Glycerol-Based Fuel Oxygenates for Biodiesel and Diesel Fuel Blends

Glycerol (1,2,3-propanetriol or glycerine) is a trihydric alcohol. It is a colorless, odorless, sweet-tasting, syrupy liquid. It melts at 291 K, boils with decomposition at 563 K, and is miscible with water and ethanol (Perry and Green, 1997). The chemical formula for glycerol is $\text{OH}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{OH}$. Glycerol is present in the form of its esters (triglycerides) in vegetable oils and animal fats.

As early as 2800 BC, glycerol was isolated by heating fats in the presence of ash (to produce soap) and as an industrial chemical. Since the late 1940s, glycerol has been produced from epichlorohydrin obtained from propylene as large chemi-

cal companies forecasted a glycerol shortage and initiated its synthetic production (Pagliaro *et al.*, 2007). The global glycerine market is estimated to be 750,000–800,000 metric tons *per year* (Spooner-Wyman and Appleby, 2003).

Glycerol cannot be added directly to fuel because at high temperatures it polymerizes and it is partly oxidized to toxic acrolein (Noureddini *et al.*, 1998). Glycerol must be modified to fuel oxygenate derivatives using as additive in diesel and biodiesel fuel blends. The most obvious derivative of glycerol has an analogy in gasoline reformulation. Oxygenated gasolines are well recognized and the demand for methyl tertiary butyl ethers (MTBEs) has grown to an estimated 473,000 barrels *per day* worldwide (Saunders, 1997). Glycerol tertiary butyl ether (GTBE) may similarly be used for diesel and biodiesel reformulation.

Glycerol is a byproduct obtained during the production of biodiesel. As the biodiesel production is increasing exponentially, the crude glycerol generated from the transesterification of vegetable oils has also been generated in a large quantity (Pachauri and He, 2006). With the increasing production of biodiesel a glut of glycerol has been created, causing market prices to plummet. This situation warrants finding alternative uses for glycerol. Glycerol is directly produced with high purity levels (at least 98%) by biodiesel plants (Ma and Hanna, 1999; Bournay *et al.*, 2005). Research efforts to find new applications of glycerol as a low-cost feedstock for functional derivatives have led to the introduction of a number of selective processes for converting glycerol into commercially valued products (Pagliaro *et al.*, 2007). The principal by-product of biodiesel production is the crude glycerol, which is about 10%wt of vegetable oil. For every 9 kg of biodiesel produced, about 1 kg of a crude glycerol byproduct is formed (Dasari *et al.*, 2005).

Oxygenated compounds such as methyl tertiary butyl ether (MTBE) are used as valuable additives as a result of their antidetonant and octane-improving properties. In this respect, glycerol tertiary butyl ether (GTBE) is an excellent additive with a large potential for diesel and biodiesel reformulation.

Glycerol can be converted into higher value products. The products are 1,3-propanediol, 1,2-propanediol, dihydroxyacetones, hydrogen, polyglycerols, succinic acid, and polyesters. Main glycerol-based oxygenates are 1,3-propanediol, 1,2-propanediol, propanol, glycerol tert-butyl ethers, ethylene glycol, and propylene glycol.

In an earlier study, glycerol was pyrolyzed for the production of clean fuels such as H_2 or a feedstock such as syngas for additional transportation fuel *via* Fischer–Tropsch synthesis. The pyrolysis of glycerol was carried out at various flow rates of N_2 (30–70 mL/min), temperatures (650–800°C), and types and sizes of packing material in a tubular reactor at atmospheric pressure. The products were mostly gas, essentially consisting of CO , H_2 , CO_2 , CH_4 and C_2H_4 (Valliyappan *et al.*, 2007). Given the highly reduced nature of carbon in glycerol and the cost advantage of anaerobic processes, fermentative metabolism of glycerol is of special interest (Yazdani and Gonzalez, 2007). Glyceride esters have been enzymatically synthesized in solvent-free system (Freitas *et al.*, 2007). The influence of important factors that affect the synthesis of glyceride esters were found to be glycerol/fatty acid molar ratio, lipase source and activating agent of the support obtained by the sol-gel technique.

4.8.1.1 Glycerol Alkyl Ethers (GAE)

Glycerol alkyl ethers (GAEs) are easily synthesized using glycerol that is reacted with isobutylene in the presence of an acid catalyst, and the yield is maximized by carrying out the reaction in a two-phase reaction system, with one phase being a glycerol-rich polar phase (containing the acidic catalyst), and the other phase being an olefin-rich hydrocarbon phase from which the product ethers can be readily separated (Gupta, 1995). On the other hand, if the reaction is carried out over an amberlyst resin, methanol in the crude glycerol must be removed to avoid catalyst poisoning. The best results were obtained for catalyst loading >5 wt%, 1–2 h of reaction time and a glycerol to isobutylene ratio of approximately 3. Lower temperatures (353 K) under these conditions resulted in a higher concentration of di- and tri-ethers and lower byproduct concentrations (Noureddini *et al.*, 1998). The optimization of glycerol ether formulations based on the results of engine tests is currently being carried out in Europe and in the US, where recently also dibutoxy glycerol was shown to act as an excellent fuel oxygenate (Sponner-Wyman and Appleby, 2003).

The etherification of glycerol with *tert*-butanol has been studied by Klepacova *et al.* (2003) at the presence of catex Amberlyst 15 as a catalyst. The maximum conversion of glycerol near 96% was reached at the temperature 363 K and at the molar ratio *tert*-butanol/glycerol = 4:1 after 180 min (Klepacova *et al.*, 2003). The etherification of glycerol with isobutylene or *tert*-butyl alcohol without solvent in the liquid phase catalyzed by strong acid ion-exchange resins of Amberlyst type and by two large-pore zeolites H-Y (Si/Al = 15) and H-BEA (Si/Al = 12.5) has been studied. The reaction of glycerol with *tert*-butyl alcohol in the liquid phase on acid Amberlyst-type ion exchange resins has been studied (Klepacova *et al.*, 2006). The best results of glycerol *tert*-butylation by isobutylene at 100% conversion of glycerol with selectivity to di- and tri-ethers larger than 92% were obtained over strong acid macroreticular ion-exchange resins. Glycerol *tert*-butyl ethers (GTBEs) or mono-, di- and tri-*tert*-butyl ethers of glycerol are potential oxygenates to diesel fuel (Klepacova *et al.*, 2005).

The preparation of the glycerol alkyl ethers (GAE) by etherification (o-alkylation) by alkenes, and preferentially by isobutylene, is one of the possibilities of glycerol usage. The GAEs can be also obtained from alkenes with C₄-fraction from pyrolysis and fluid catalytic cracking at the presence of the acid catalyst. A mixture of mono-, di- and tri-alkyl glycerol ethers can be produced. These ethers (mainly di- and tri-alkyl glycerols) are the main products of glycerol etherification reaction and are excellent oxygen additives for diesel fuel (Jamroz *et al.*, 2007). The addition of these ethers has a positive effect on the combustion of diesel fuel (high cetane number, CN), and preferentially ethers are active by reduction of fumes and particulate matters, carbon oxides, and carbonyl compounds in exhausts (Klepacova *et al.*, 2003).

In particular, a mixture of 1,3-di-, 1,2-di-, and 1,2,3-tri-*tert*butyl glycerol, when incorporated in standard 30–40% aromatic-containing diesel fuel, leads to signifi-

cantly reduced emissions of particulate matter, hydrocarbons, carbon monoxide, and unregulated aldehydes (Kesling *et al.*, 1994).

4.8.1.2 Propylene Glycol

Glycerol can be converted to propylene glycol (1,2-propanediol) by dehydration followed by hydrogenation (hydrogenolysis) reaction. Propylene glycol is used in an antifreeze mixture (70% propylene glycol and 30% glycerol) that can be produced, refined, and marketed directly by existing biodiesel facilities. The method is based on hydrogenolysis of glycerol over a copper chromite catalyst at 475 K (Pagliaro *et al.*, 2007).

The reaction pathway proceeds *via* an acetol (hydroxyacetone) intermediate in a two-step process. The first step of forming acetol occurs at atmospheric pressure, while subsequent hydrogenation at 475 K and 10 bar hydrogen gas eventually affords propylene glycol in 73% yield at significantly lower cost than propylene glycol made from petroleum. A main advantage of the process is that the copper-chromite catalyst can be used to convert crude glycerol without further purification (Pagliaro *et al.*, 2007).

4.8.2 P-series Fuels

P-series fuel is a unique blend of liquefied petroleum gas liquids, ethanol, hydrocarbons, and methyltetrahydrofuran (MeTHF). P-series fuels are blends of ethanol, MeTHF, and pentanes, with butane added for blends that would be used in severe cold-weather conditions to meet cold start requirements. P-series fuel is made primarily from biorenewable resources and provides significant emissions benefits over reformulated gasoline. P-series fuel can be mixed with gasoline in any proportion and used in flexible fuel vehicles. P-series fuels are clear, colorless, 89–93 octane, liquid blends that are formulated to be used in flexible fuel vehicles (FFVs). Like gasoline, low vapor pressure formulations are produced to prevent excessive evaporation during summer and high vapor pressure formulations are used for easy starting in winter. P-series fuel is at least 60% non-petroleum. It also has many environmental benefits. Because a majority of the components that make up P-series fuels comes from domestically produced renewable resources, this alternative fuel promotes both energy security and environmental quality. P-series fuels could be 96% derived from domestic resources. P-series fuels could reduce fossil energy use by 49% to 57% and petroleum use by 80% relative to gasoline. Greenhouse gas emissions from the production and use of P-series are substantially better than those from gasoline. Each unit of P-series fuel emits approx 50% less carbon dioxide, 35% less hydrocarbons, and 15% less carbon monoxide than gasoline. It also has 40% less ozone forming potential.

4.8.3 *Dimethyl Ether (DME)*

Dimethyl ether (DME or $\text{CH}_3\text{--O--CH}_3$), is a new fuel that has attracted much attention recently. Today, DME is made from natural gas, it can also be produced by gasifying biomass. DME can be stored in liquid form at 5–10 bar pressure at normal temperature. A major advantage of DME is its naturally high cetane number, which means that self-ignition is easier. The high cetane rating makes DME the most suitable for use in diesel engines, which implies that the high level of efficiency of the diesel engine is retained when using DME. The energy content of DME is lower than in diesel.

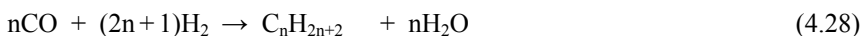
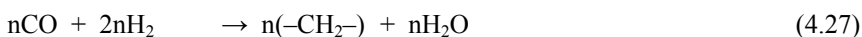
DME can be produced effectively from biosyngas in a single-stage, liquid phase (LPDME) process. The origin of syngas includes a wide spectrum of feedstocks such as coal, natural gas, biomass, and others. Non-toxic, high density, liquid DME fuel can be easily stored at modest pressures. The production of DME is very similar to that of methanol. DME conversion to hydrocarbons, lower olefins in particular, is being studied using ZSM-5 catalysts with varying $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios, whereas the DME carbonization reaction to produce methyl acetate is studied over a variety of group VIII metal substituted heteropolyacid catalysts.

4.8.4 *Fischer–Tropsch (FT) Liquid Fuel from Biomass*

Fischer–Tropsch (FT) liquid fuel can be used as alternate diesel fuel. The FT catalytic conversion process can be used to synthesize diesel fuels from a variety of feedstocks, including coal, natural gas and biomass. The alternate fuel source is coal, indirectly converted to diesel fuel. The FT process uses various catalysts to produce linear hydrocarbons and oxygenates, including unrefined gasoline, diesel, and wax ranges.

Synthetic FT diesel fuels can have excellent autoignition characteristics. FT diesel is composed of only straight chain hydrocarbons and has no aromatics or sulfur. Reaction parameters are temperature, pressure, and H_2/CO ratio. FT product composition is strongly influenced by the catalyst composition: the yield of paraffins is higher with cobalt catalytic runs, and the yield of olefins and oxygenates is higher with iron catalytic runs.

Basic FT reactions are:



Catalysts and reactors have been extensively investigated for liquid phase Fischer–Tropsch synthesis (Davis, 2002). Synthetic Fischer–Tropsch diesel fuel can provide benefits in terms of both PM and NO_x emissions (May, 2003). Properties of FT and No. 2 diesel fuels are given in Table 4.46.

Table 4.46 Properties of Fischer–Tropsch (FT) diesel and No. 2 diesel fuels

Property diesel	Fischer–Tropsch diesel	No. 2 petroleum
Density, g/cm ³	0.7836	0.8320
Higher heating value, MJ/kg	47.1	46.2
Aromatics, %	0–0.1	8–16
Cetane number	76–80	40–44
Sulfur content, ppm	0–0.1	25–125

FT is most compatible with existing distribution for conventional diesel and only minimal adjustments are required to obtain optimal performance from existing diesel engines. Physical properties of FT are very similar to No. 2 diesel fuel, and its chemical properties are superior in that the FT process yields middle distillates that, if correctly processed (as through a cobalt-based catalyst), contain no aromatics or sulfur compounds.

4.8.5 Other Bio-oxygenated Liquid Fuels

Methanol and ethanol are not the only transportation fuels that might be made from wood. A number of possibilities exist for producing alternatives. The most promising bio-oxygenated fuels, and closest to being competitive in current markets without subsidy, are ethanol, methanol, ethyl-tert-butyl ether, and methyl-tert-butyl ether. Other candidates include isopropyl alcohol, sec-butyl alcohol, tert-butyl alcohol, mixed alcohols, and tert-amylmethyl ether.

Ethanol or grain alcohol is not restricted to grain as a feedstock. It can be produced from other agricultural crops and lignocellulosics such as wood. It has often been advocated as a motor fuel, and has been used frequently in times of gasoline scarcity.

Besides comparisons in production costs, there is a question whether ethanol at the same price *per* gallon as gasoline is of equal value. The heating value of ethanol is less, only 76,500 BTUs *per* gallon as compared to 124,800 for gasoline. However, ethanol is a higher octane number than gasoline, and for that reason it might attain about the same mileage *per* gallon as gasoline. The octane number is a value used to indicate the resistance of a motor fuel to knock. Octane numbers are based on a scale on which isooctane is 100 (minimal knock) and heptane is 0 (bad knock). We are therefore assuming a gallon of gasoline and a gallon of ethanol to be of equal value.

Another possibility for bio-oxygenated fuels is methanol. Methanol could conceivably be made from grain, but its most common source is natural gas. Use of natural gas is better for reducing carbon dioxide production in comparison to other fossil fuels, but use of renewable fuels instead of natural gas would be better still. It can be made from coal or wood with more difficulty and lower efficiency than from natural gas. The cost of making methanol from natural gas is around \$0.40 *per* gallon. It could probably be sold as a motor fuel for about \$0.60–\$0.70 *per* gallon. This would be equivalent to gasoline selling at about \$0.92–\$1.03 *per* gallon. Methanol was

once produced from wood as a byproduct of charcoal manufacture, but overall yields were low. To produce methanol from wood with a significantly higher yield would require production of synthesis gas in a process similar to that used for production of methanol from coal. Such processes for gasifying wood are less fully developed than the two-stage hydrolysis process for the production of ethanol.

The high-octane rating is characteristic of all oxygenated fuels, including ethanol, methanol, ethyl-tert-butyl ether, and methyl-tert-butyl ether (MTBE). MTBE is made by reacting isobutylene with methanol. Ethyl-tert-butyl ether (ETBE) is made by using ethanol instead of methanol. Thus either ethanol or methanol from either grain or wood could be a factor in making tert-butyl ether octane enhancers. The characteristics of ethers are generally closer to those of gasoline than those of alcohols. Ethers are benign in their effect on fuel system materials and are miscible in gasoline; therefore, they are not subject to phase separation in the presence of water, as are methanol and ethanol.

Alternative fuels from wood, as well as grain, have a potential for being competitive with gasoline and diesel motor fuels from petroleum, even without subsidization. For ethanol to compete directly, without subsidy, oil would probably have to sell for \$40 or more *per* barrel. However, the environmental and octane-enhancing benefits of ethanol and other oxygenated fuels that may be produced from grain and wood may make them worth more than comparisons on fuel value alone would indicate.

Diesel fuels or gasoline from wood are possibilities through a number of approaches. The Fischer–Tropsch pyrolysis process, used successfully for converting coal to synthesis gas in South Africa could also be used to make synthesis gas from wood. Synthesis gas could then be used to make gasoline or diesel fuel. Or methanol could be produced from wood and then, by a catalyzed reaction known as the Mobil process, be transformed to gasoline.

In the two-stage hydrolysis process, for every 100 kg of oven dry wood feedstock about 20 kg carbohydrates suitable for processing to ethanol are obtained from the second stage. There are more carbohydrates derived from the first stage, about 24.9 kg, but many of these first stage carbohydrates are not necessarily fermentable to ethanol. Ethanol is a possibility if xylose can be fermented to ethanol economically. Fermentation of the xylose and glucose from the first stage could result in almost doubling the ethanol production as compared to only fermenting the glucose from the second stage. Other possible products from the first stage carbohydrates are single-cell protein, furfural, and feed molasses.

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